Multifunctional (Nano)Composite Materials for Energy Storage: *Towards Flexible Load-Bearing Batteries and Supercapacitors*

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Why Nanocomposite Electrodes?

- Ability to store energy of Li-ion batteries and supercapacitors is largely governed by the ability of their electrode materials to host high content of ions
- Many active materials exhibit outstanding ability for ion storage but suffer from some limitations (e.g. large volume changes during insertion/extraction of ions and/or low electrical and ionic conductivity)
- Rational design of carbon-containing nanocomposite electrodes allows one to overcome these limitations while still achieving up to 90 % of the theoretical energy storage

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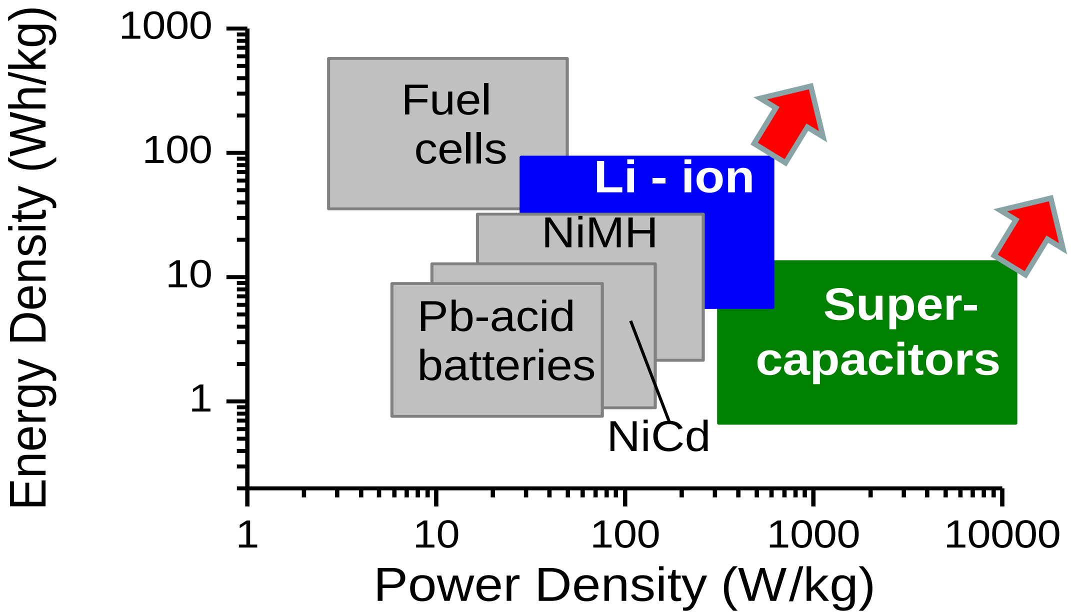
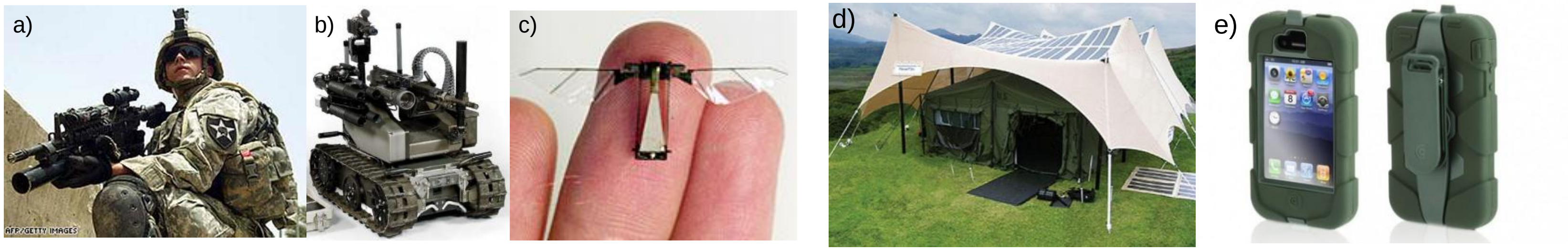
- In addition, the use of MULTI-FUNCTIONAL electrodes (e.g., with added load-bearing functionalities) has the potential to greatly reduce the overall weight of the system

Supercapacitors and Li-ion Batteries

- ✓ **Need More Energy per unit mass (and volume!) of the system**
- ✓ **Need More Power per unit mass (and volume!) of the system**



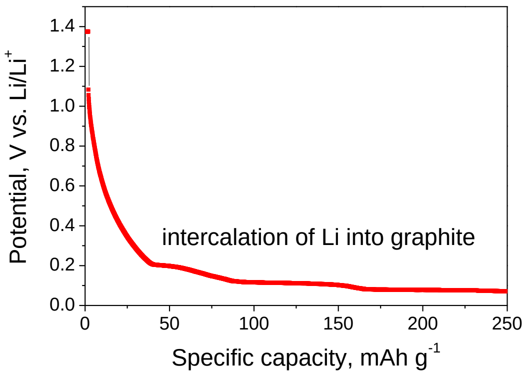


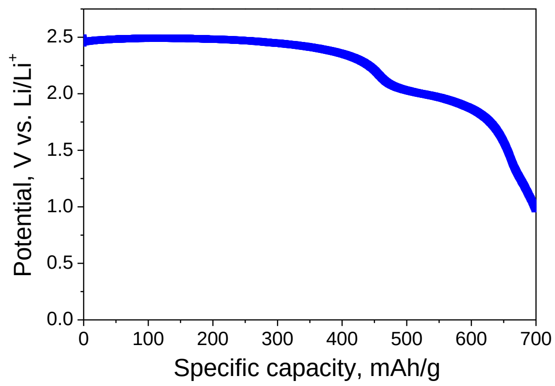
Operating Principle of Li-ion battery

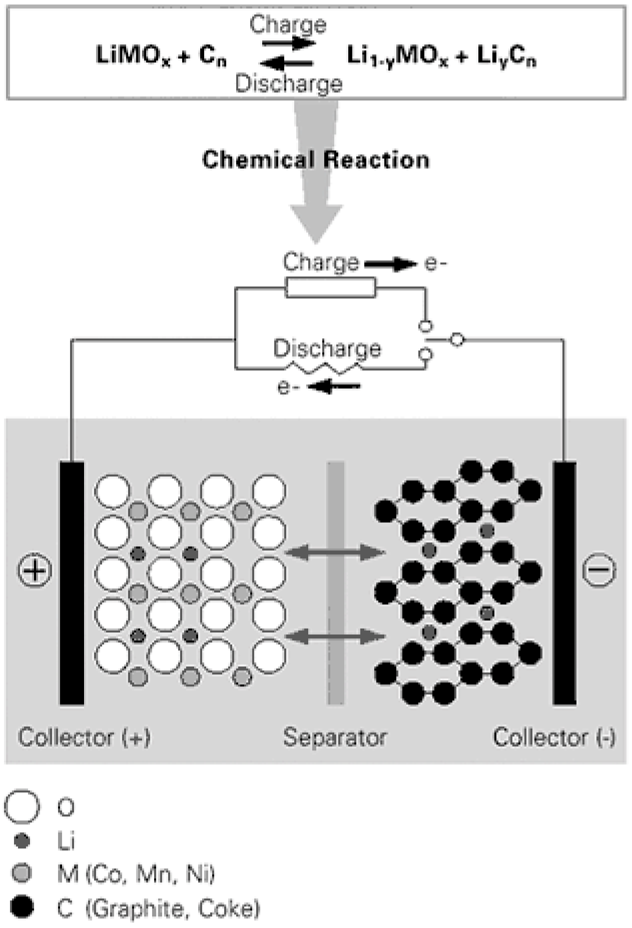
- "Rocking-chair" or "shuttlelock" mechanism: **Li ions shuttle between the anode and the cathode**

- Higher capacity of the cathode or the anode will lead to higher capacity of a battery

- The potential between the anode and the cathode determines the open circuit voltage of a Li-ion battery

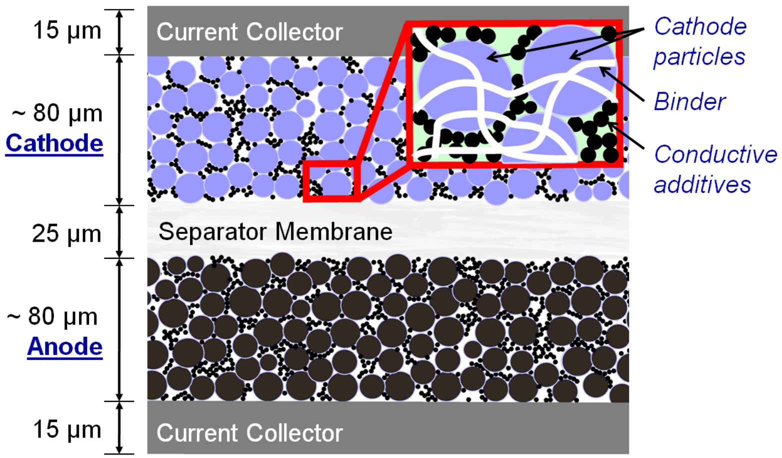


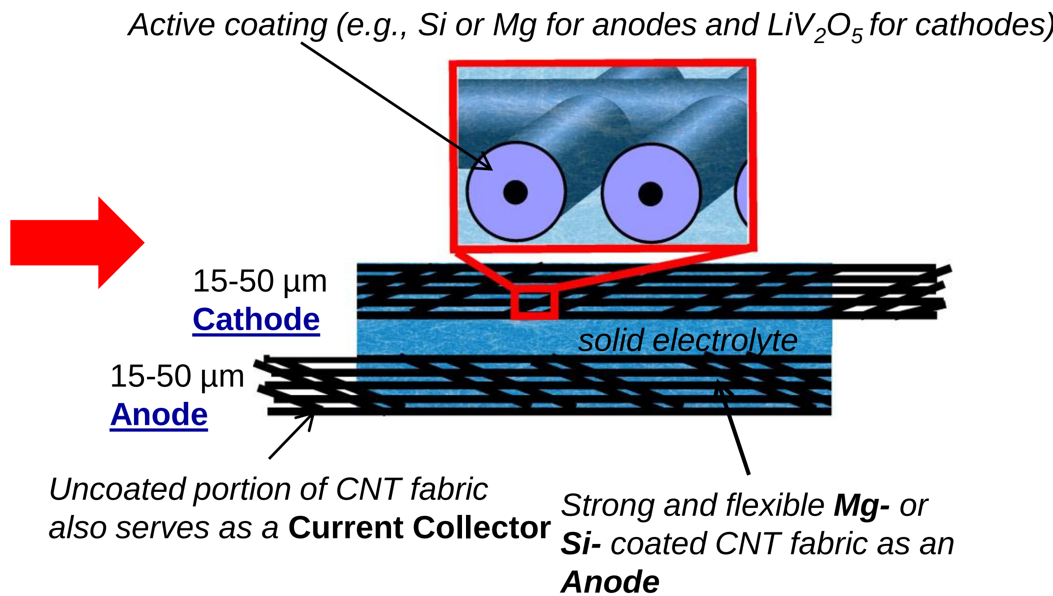




http://www.varta-automotive.com

Multifunctional Nano-Composite Fabric





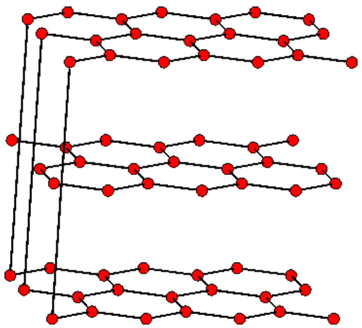
Traditional Electrodes and Cell Architecture

- Low electrical conductivity
- Low thermal conductivity
- Heavy/bulky metal foils
- No mechanical strength

Multifunctional Nano-Composite Fabric

- Ultra-High electrical conductivity
- High thermal conductivity
- No metal foil current collectors needed
- Enhanced safety *(when solid electrolyte is used)*
- High mechanical strength / multi-functionalilty

Limitations of Graphitic Anodes

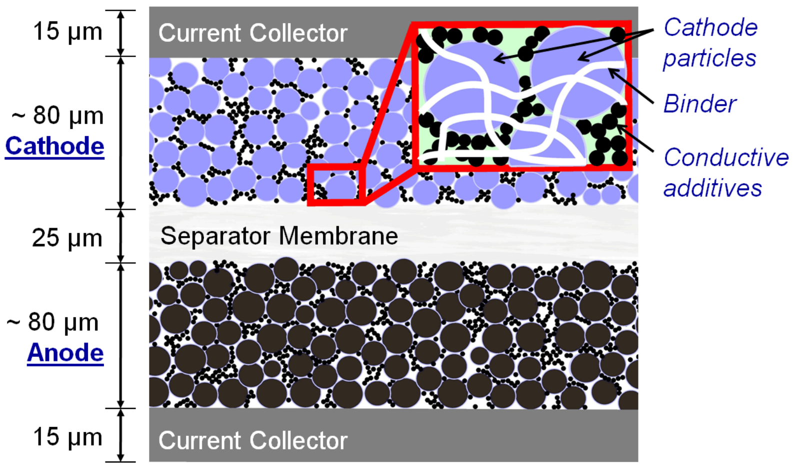


• Limited specific capacity: theoretical capacity of 374 mAh/g corresponds to **1 Li per 6 C atoms (LiC_6)**

• Most commercial graphitic anodes experience capacity of ~ 270-340 mAh/g

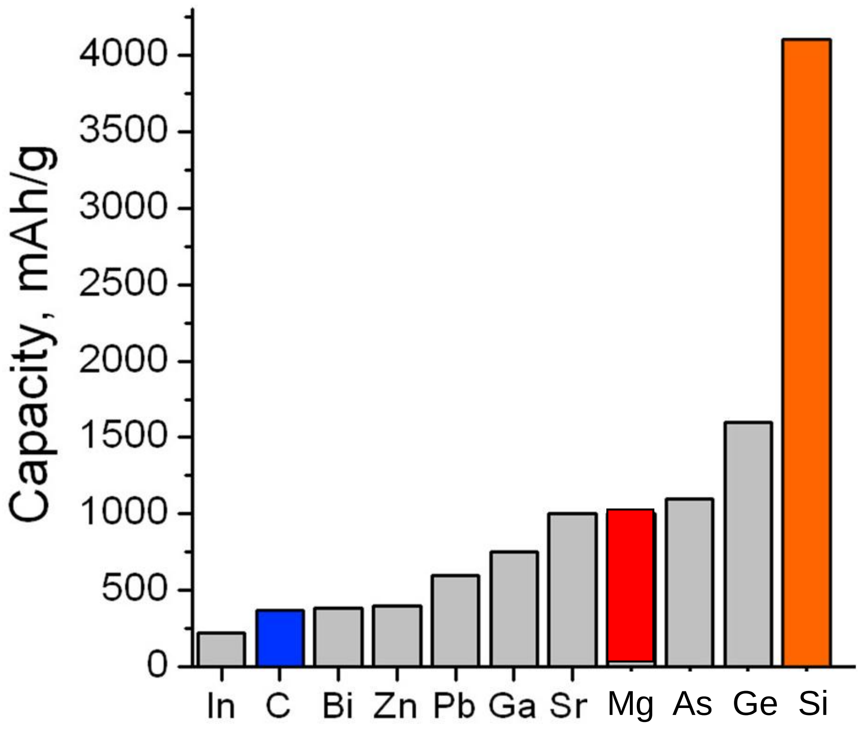
•Binder (3-8 wt. %) and current collector (Cu) add weight and thus lower the effective specific capacity to ~ 200 mAh/g, particularly for high power cells

• If graphite is replaced with Carbon fibers or CNTs, the mechanical properties of the CNT will be significantly reduced after cycling because insertion and extraction of Li between the graphene layers. Thus, multifunctionality will not be feasible with pure C anodes

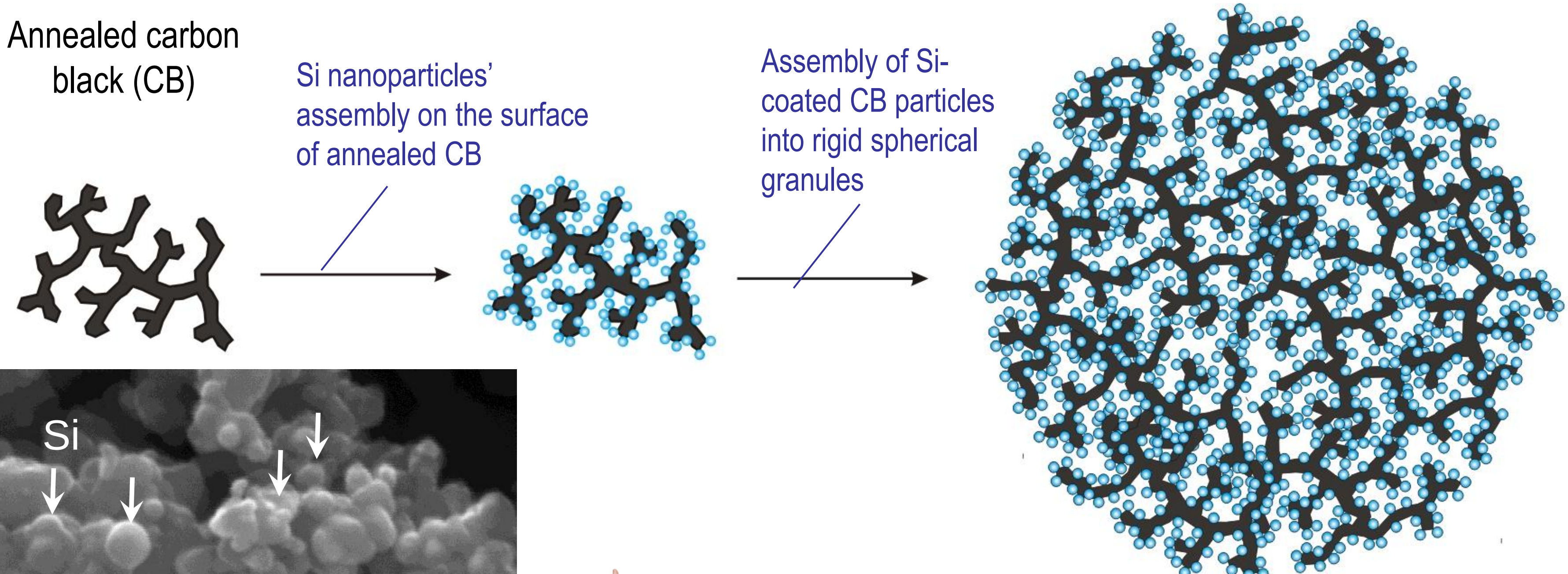


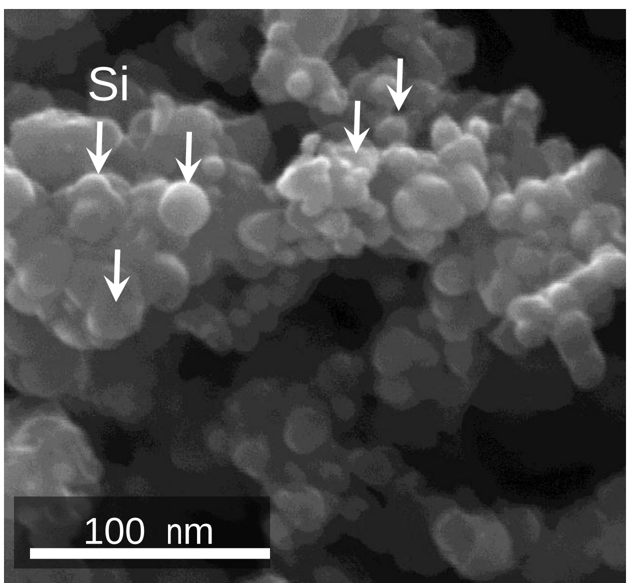
High Capacity Anodes for Li-ion Batteries

- Metals or semiconductors that alloy with Li offer much higher theoretical capacity than graphite
- Si capacity is ~ 4000 mAh/g
- **Challenges**:
  - Unless strongly lithiated, Si exhibits low electrical and low ionic conductivity
  - Large Si particles pulverize and cannot be discharged sufficiently rapidly
  - Small Si nanoparticles exhibit very large thermal and electrical resistance as well as very large specific surface area and therefore large irreversible capacity losses (low Columbic Efficiency)
  - Si expansion leads to changes in the electrode thickness and reduces SEI stability



Si-C Nanocomposites Can do Better Job Than Si



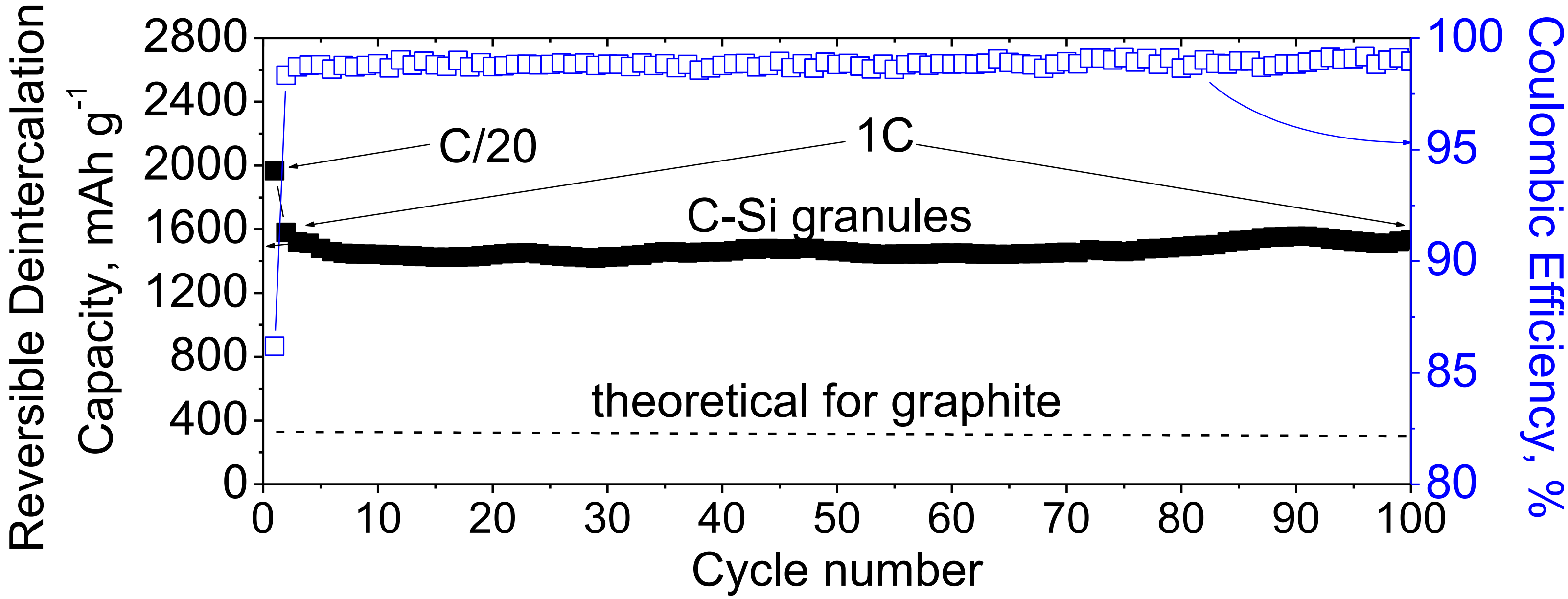


- Uniformity of the deposited Si nanoparticles
- No volume changes during Li insertion/extraction
- Compatibility with existing manufacturing technologies (drop-in replacement)
- High electrical & thermal conductivity

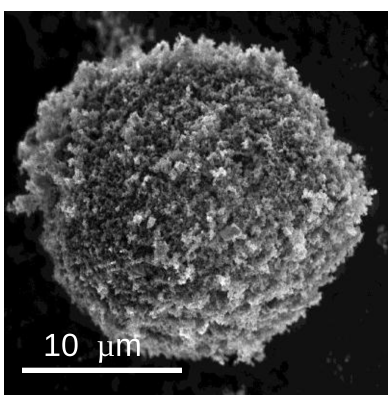
Patent pending

Magasinski, A. et. al, ***Nature Materials***, 2010, *9*, 353

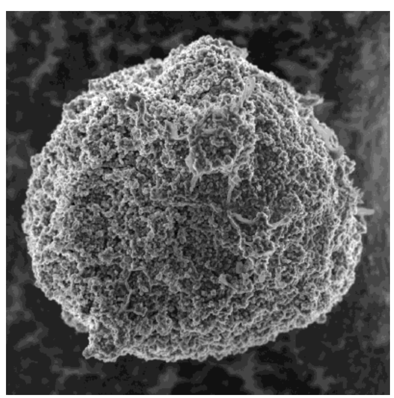
Si-C Nanocomposites Can do Better Job Than Si

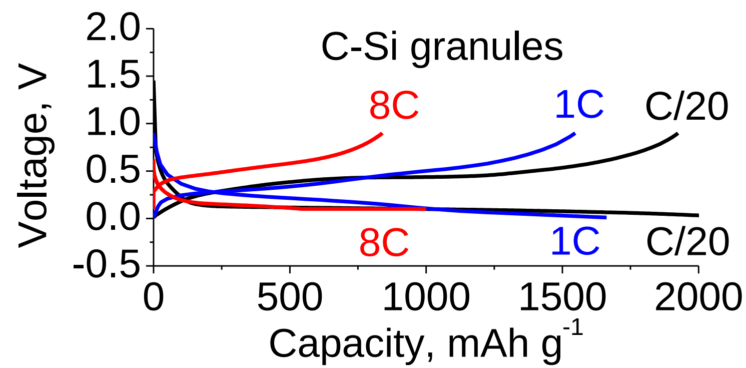


Before cycling



After





Patent pending

Magasinski, A. et. al, ***Nature Materials***, 2010, *9*, 353

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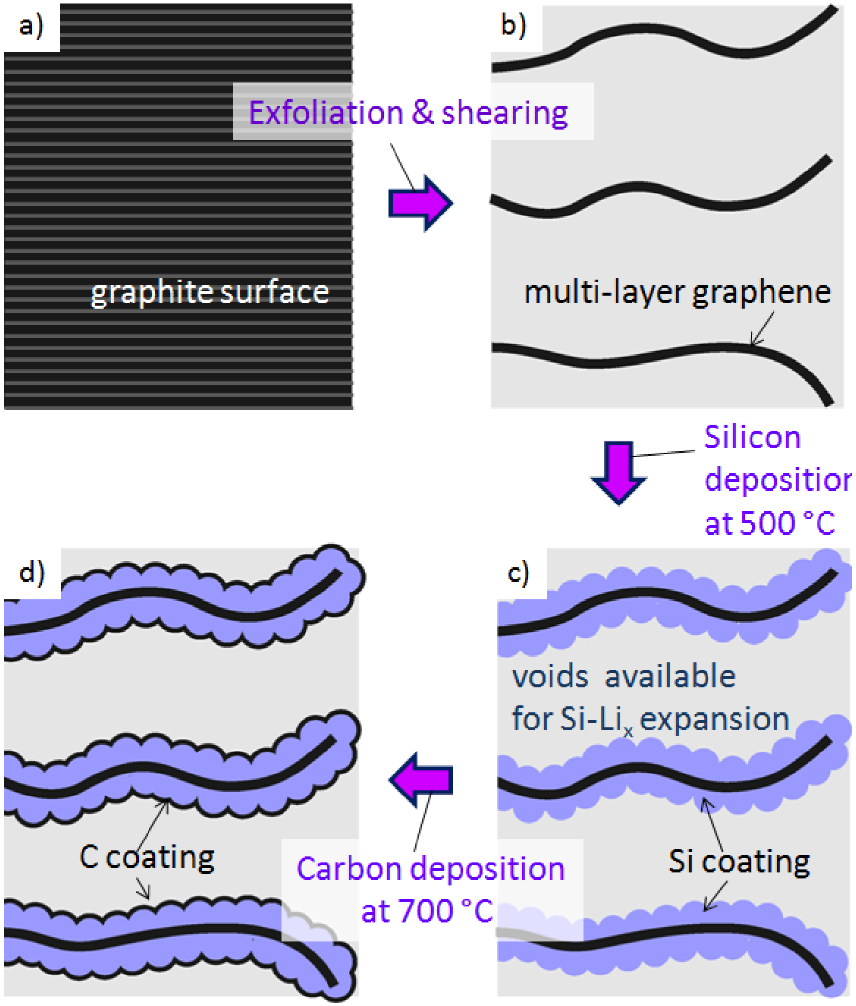
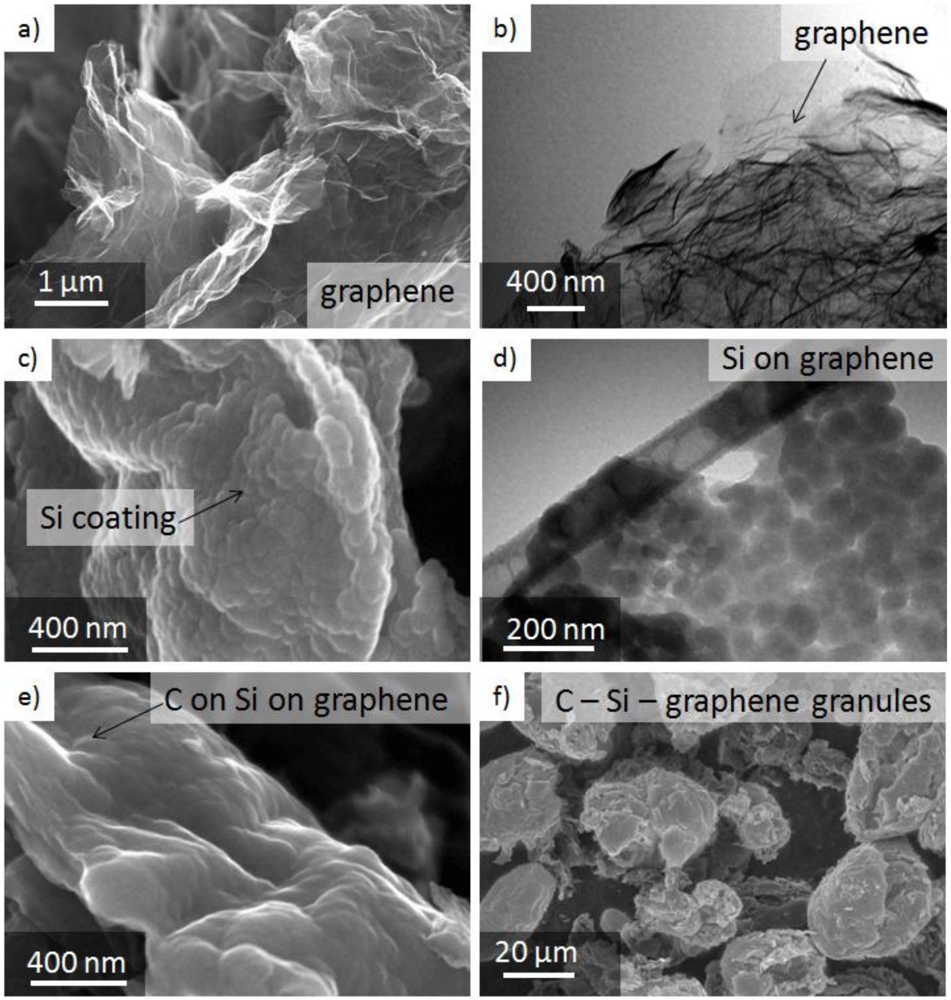
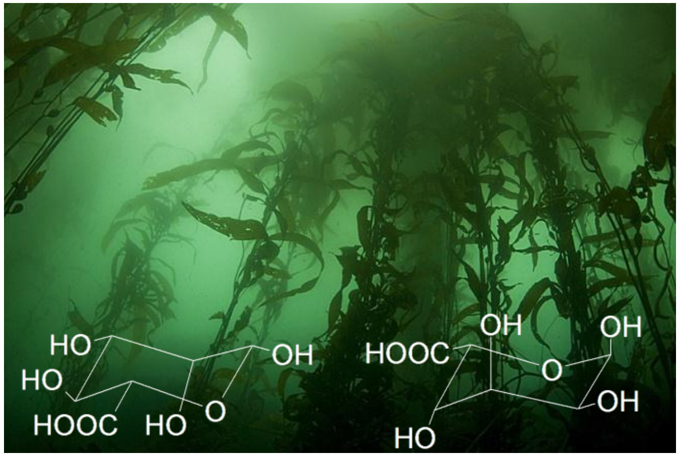


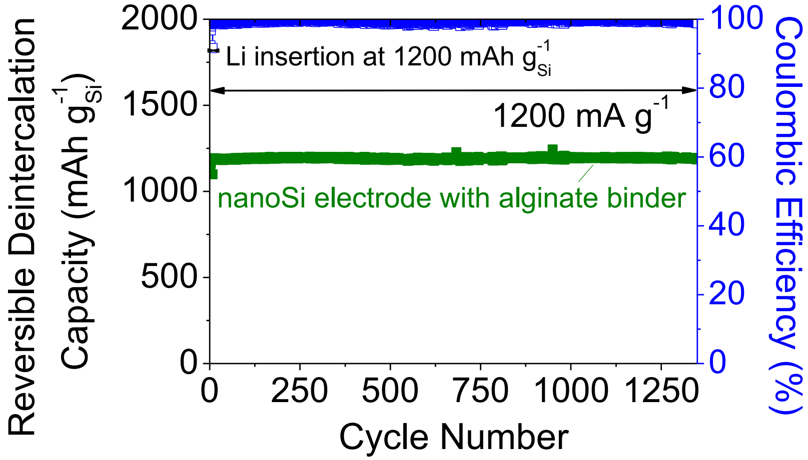


Patent pending

Evanoff, K et. al, ***Advanced Energy Materials***, v1 (4), p 495, 2011

Functional Polymer Coatings on Active Particles (e.g. on Si) May Improve Electrode Performance





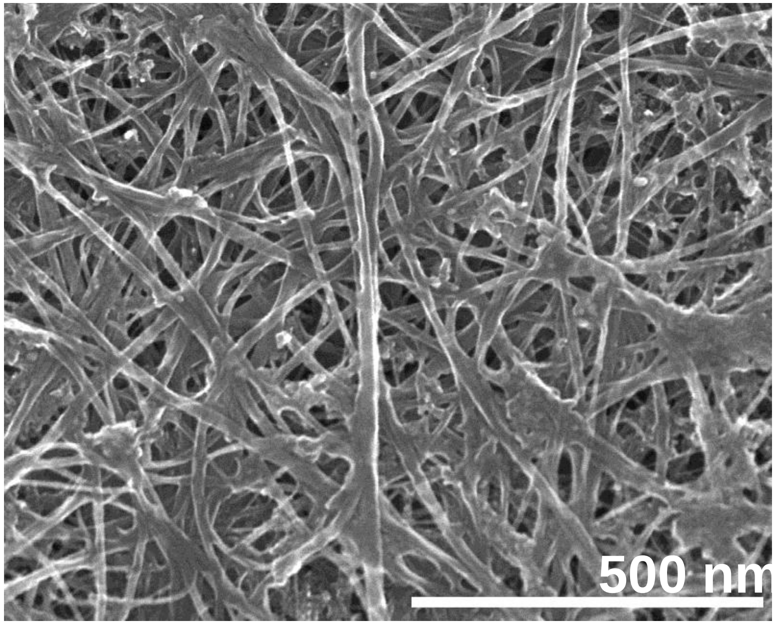
Patent pending

- Alginate is extracted from brown algae, which is: the fastest growing plant on the planet, does not need agricultural land

- Environmentally-friendly process: (a) growing algae captures CO_2 and produced O_2; (b) alginate (as a Na-alginate) is produced from brown algae by boiling it in a soda solution (no need for extensive chemical treatment; in contrast, CMC synthesis involves the alkali-catalyzed reaction of cellulose with chloroacetic acid to introduce carboxy groups); (c) solvent – water (in contrast, PVDF requires NMP)

I. Kovalenko et al., ***Science***, 2011, 7, p. 75

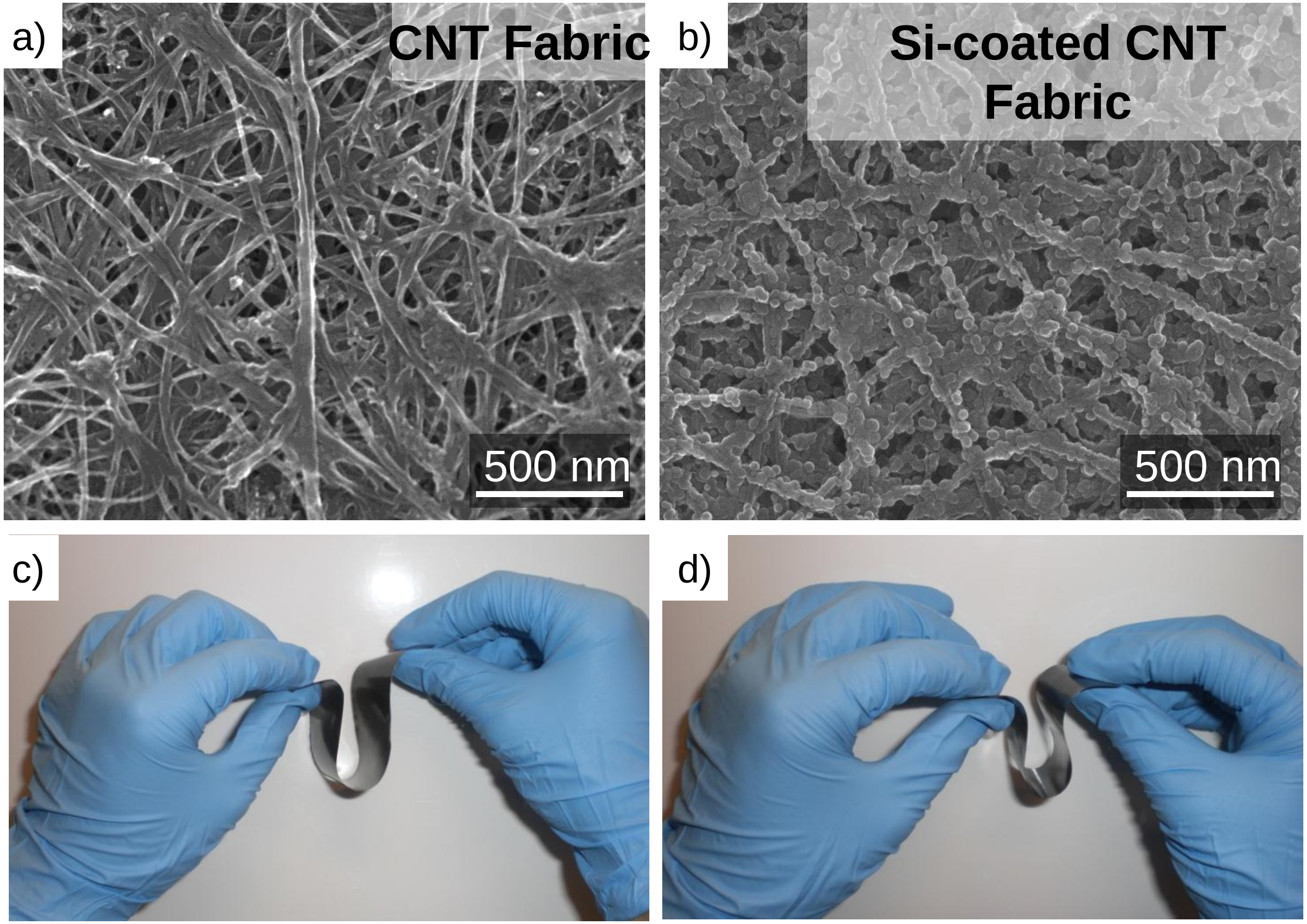
CNT fabric for Nano-Composite Anode



CNT supplied by:

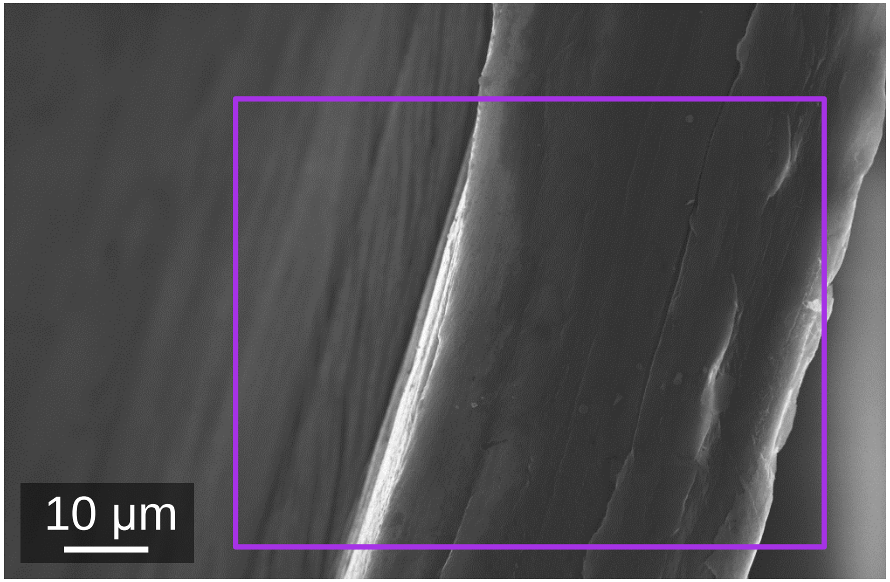
nanocomp TECHNOLOGIES, INC.

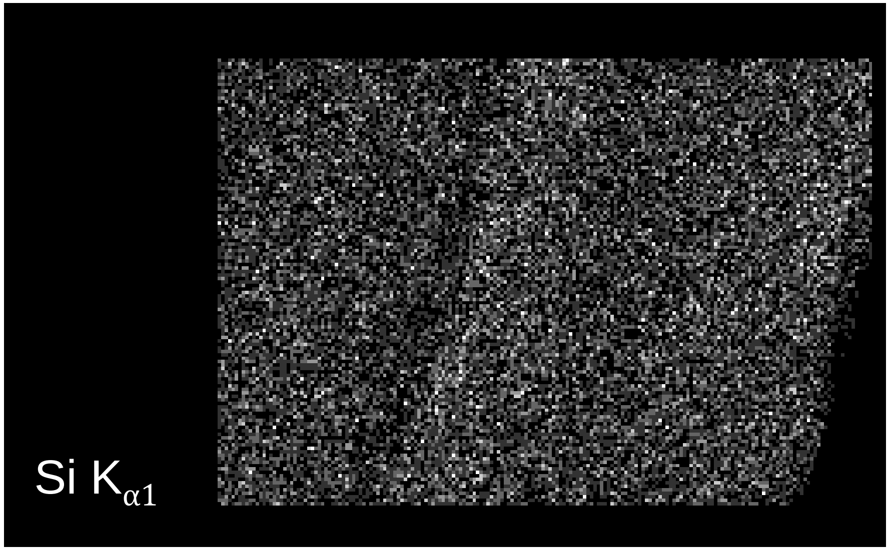
Si-C Nano-Composite Anode Fabric



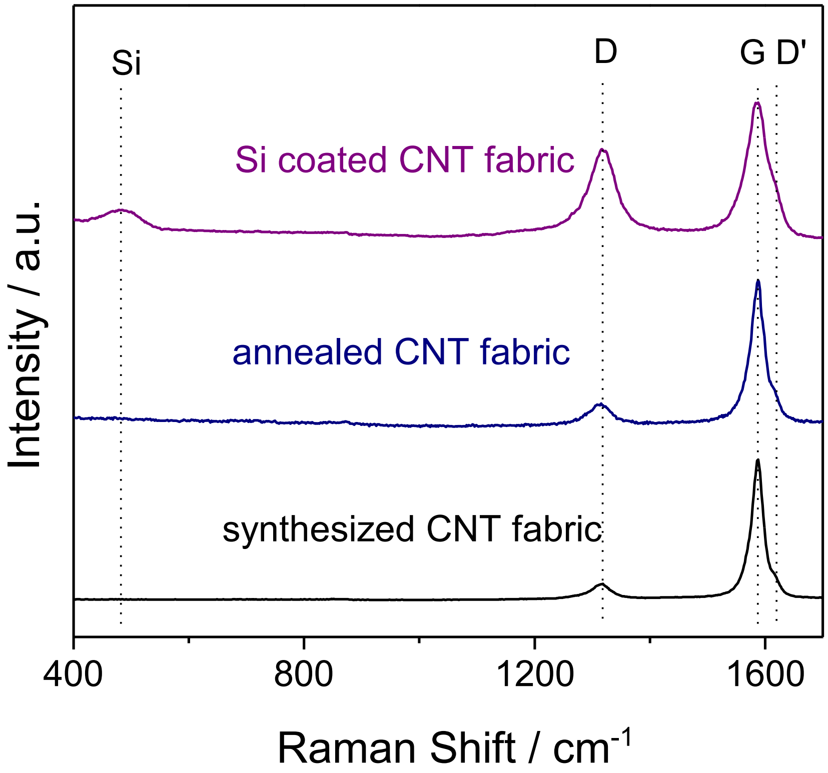
Evanoff, K. et. al, ***submitted***, 2012

Si-C Nano-Composite Anode Fabric



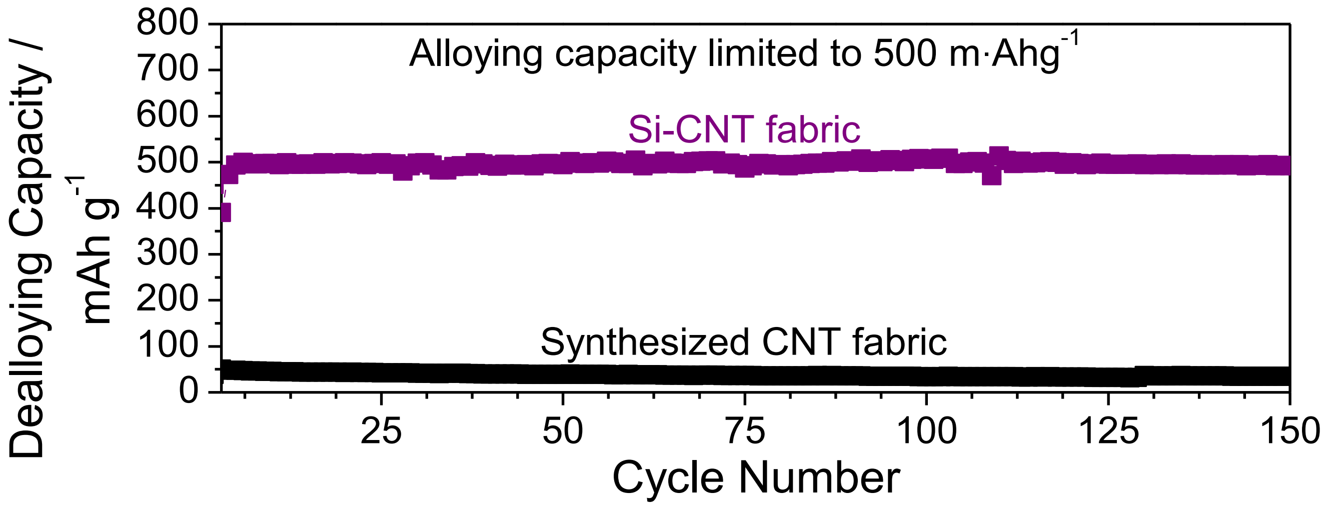


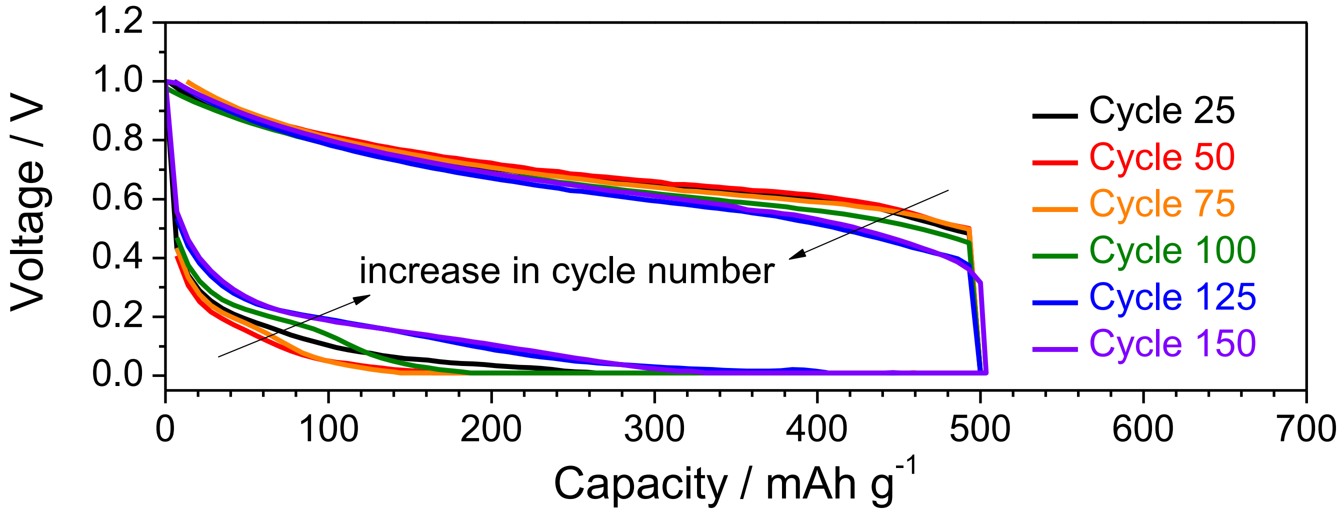
- Uniform Si deposition within the CNT-based electrode



Evanoff, K. et. al, ***submitted***, 2012

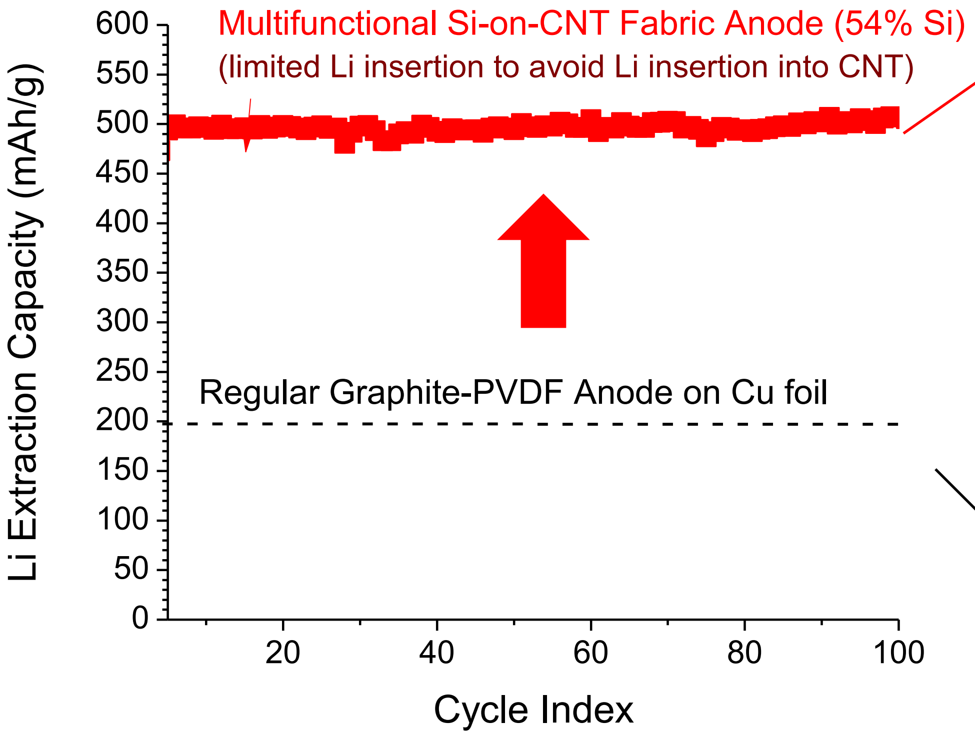
Si-C Nano-Composite Anode Fabric

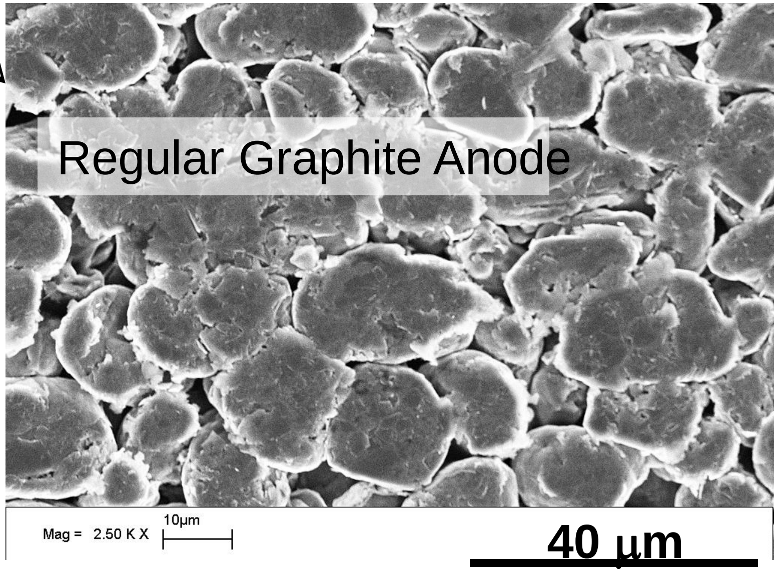




Evanoff, K. et. al, ***submitted***, 2012

Si-C Nano-Composite Anode Fabric

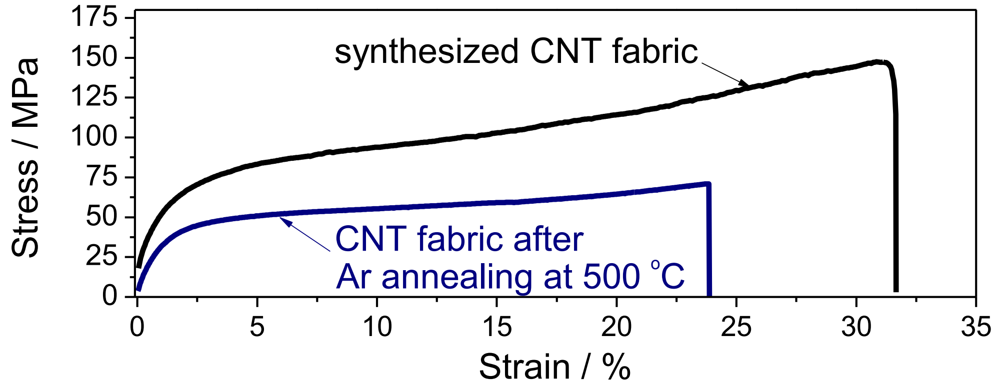




Note:
Density of 90 um Graphite coating < 1.6 g/cc (each side) ; Density of 18 um Cu = 9 g/cc

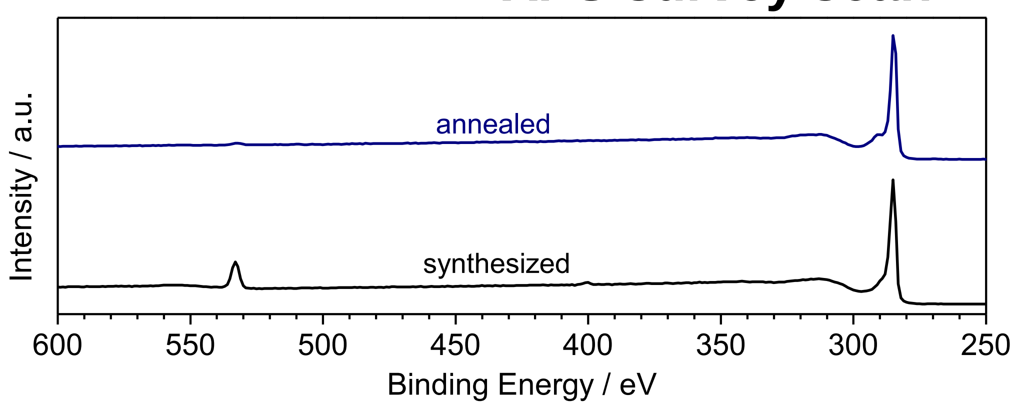
Evanoff, K. et. al, ***submitted***, 2012

CNT Fabric: Effect of Annealing *(since we deposit Si at 500 C)*

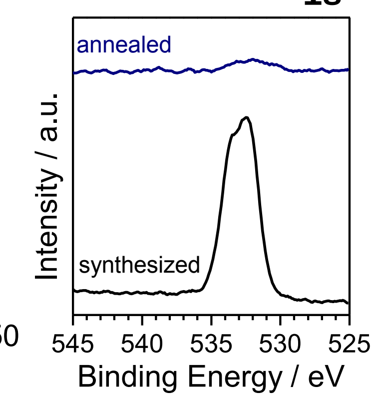


- Moderate reduction in strain and strength upon annealing in Ar at 500 C for 1h
- Likely due to reduction of the CNT-CNT bonding strengths caused by stripping some of the functional groups

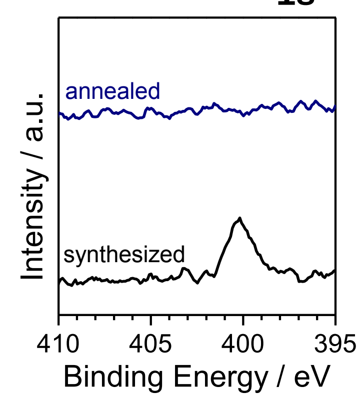
XPS survey scan



O_{1s}

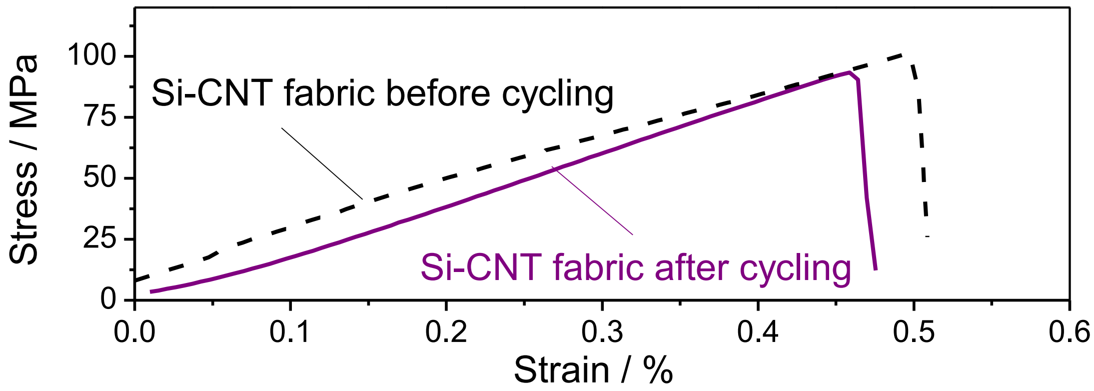


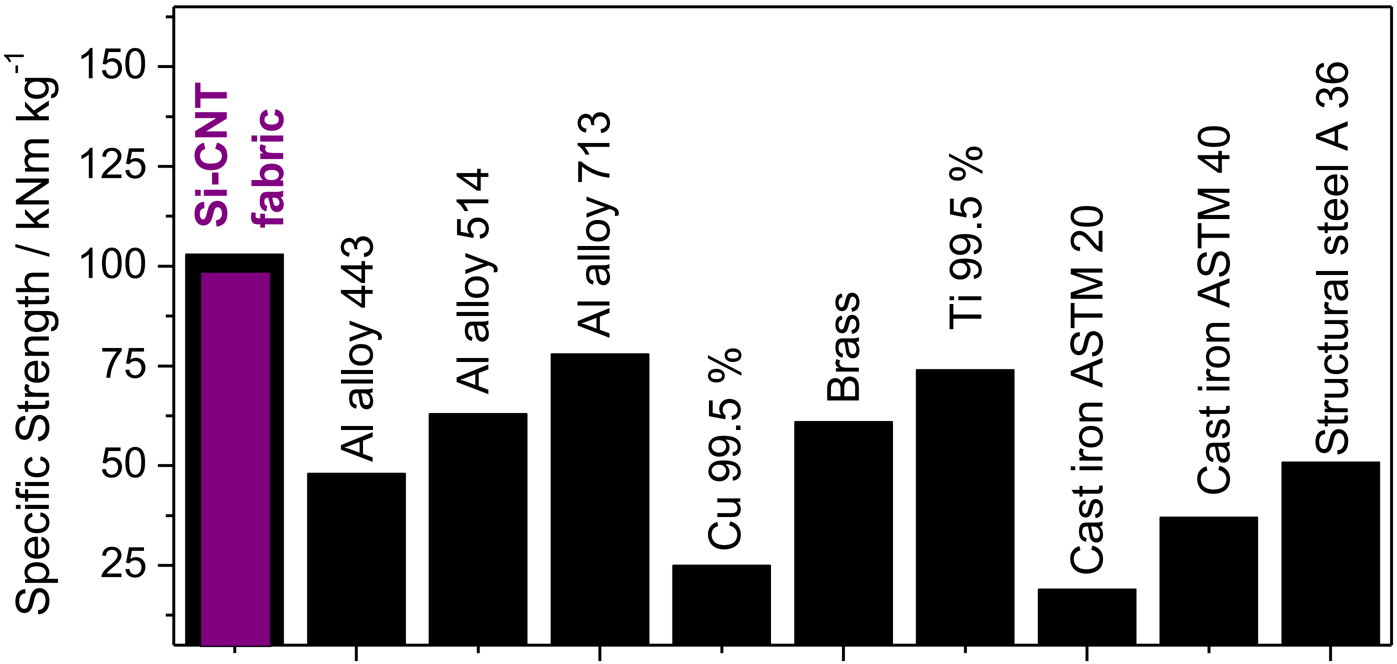
N_{1s}



Evanoff, K. et. al, ***submitted***, 2012

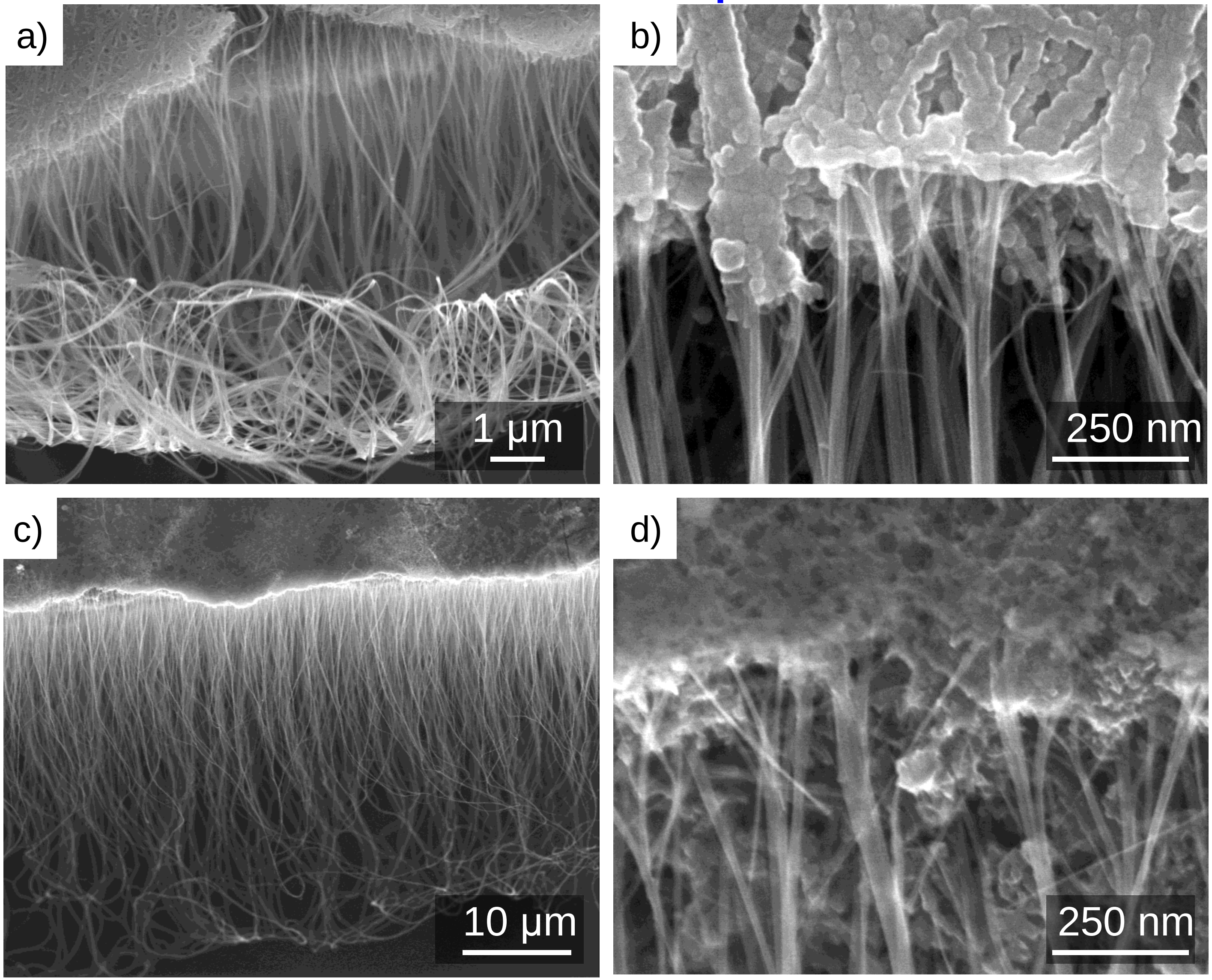
Si-C Nano-Composite Anode Fabric





Evanoff, K. et. al, ***submitted***, 2012

Si-C Nano-Composite Anode Fabric



- Pull-out Behavior

Evanoff, K. et. al, ***submitted***, 2012

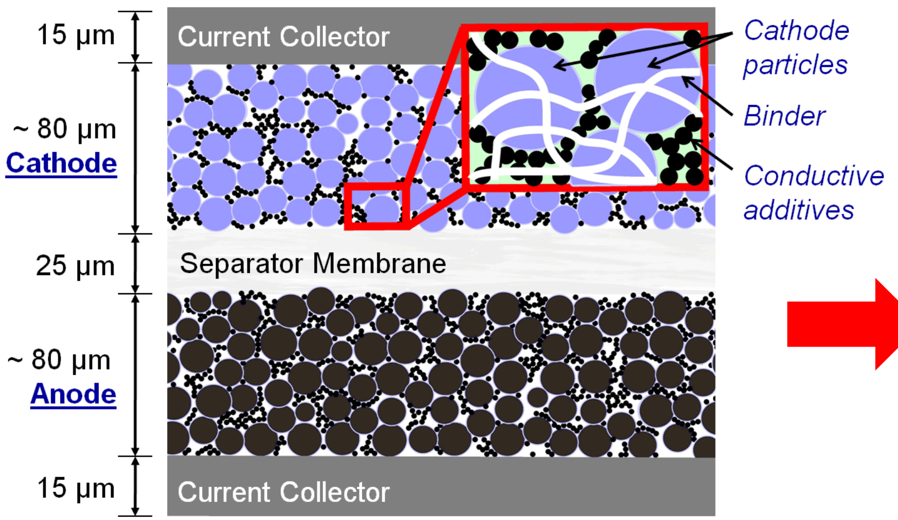
Si-C Nano-Composite Anode Fabric

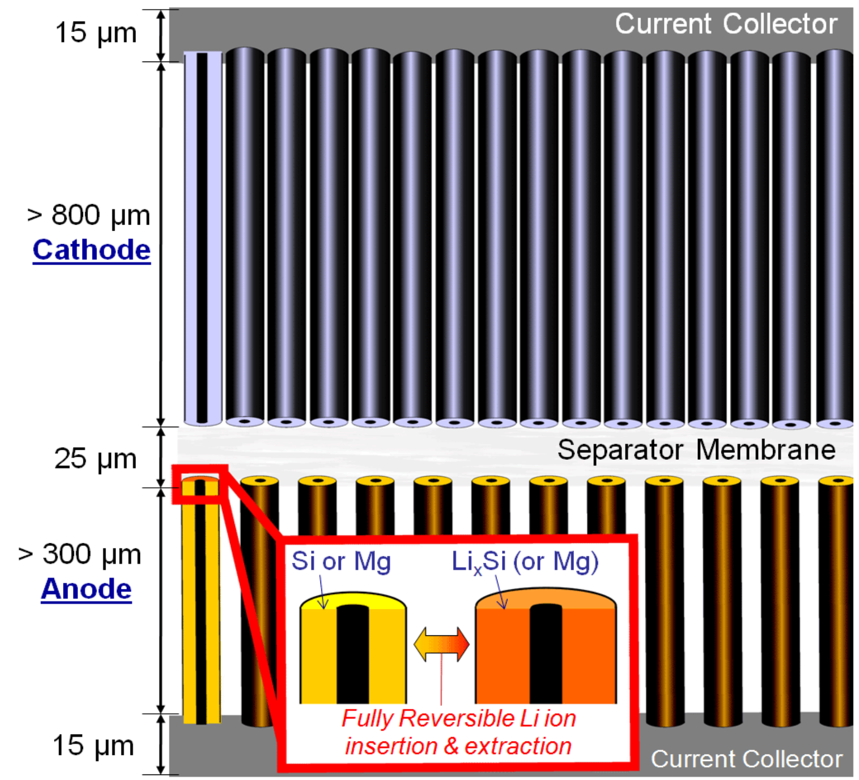
	ρ 1×10^{-3} W•cm	**K** $W•m^{-1}K^{-1}$
CNT fabric	1.17 ± 0.11	29.72 ± 3.24
Si-coated CNT fabric	2.93 ± 0.34	17.59 ± 1.95
Si nanopowder electrode	327,500 ± 22,000	0.40
Graphite electrode		1.04

- High Thermal and Electrical Conductivities
- Still likely <u>limited by the Electrode-Probe Contact Resistance</u>

Evanoff, K. et. al, ***submitted***, 2012

Vertically Aligned CNT - Based Electrodes



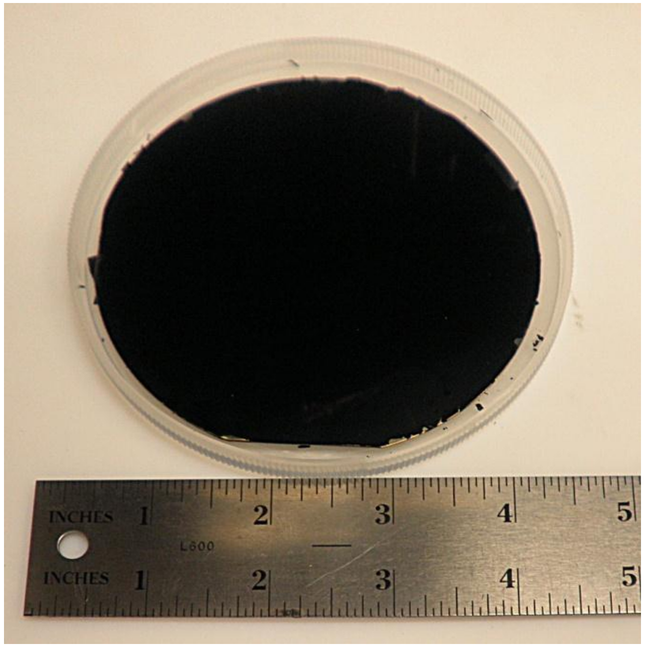


Traditional Electrodes and Cell Architecture

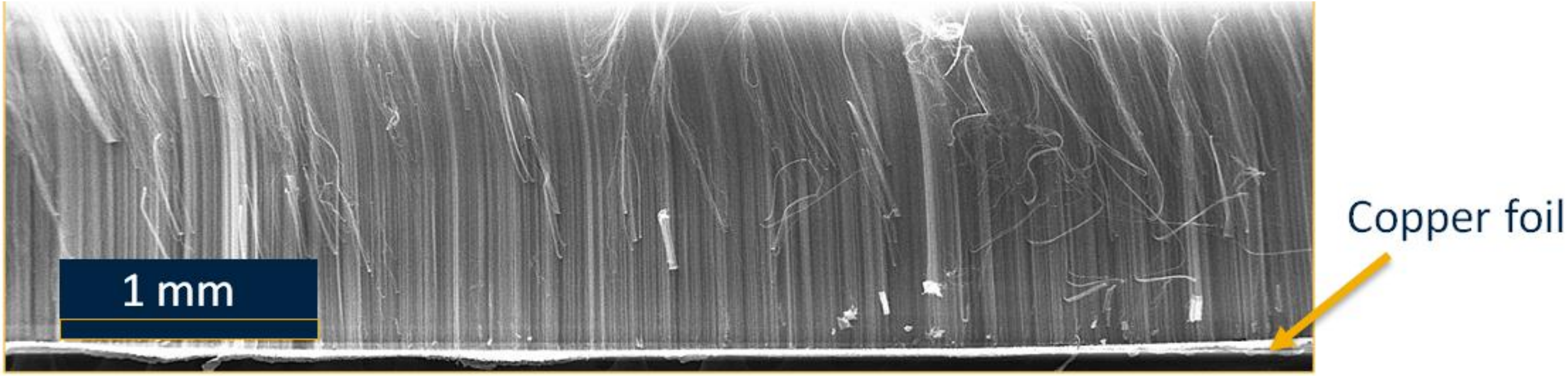
- Low electrical conductivity
- Low thermal conductivity
- Heavy/bulky metal foils

- Ultra-High electrical conductivity
- High thermal conductivity
- Thicker electrodes and thus smaller contribution of inactive components (separators, metal foils, etc.)

Multi-Walled CNT Growth



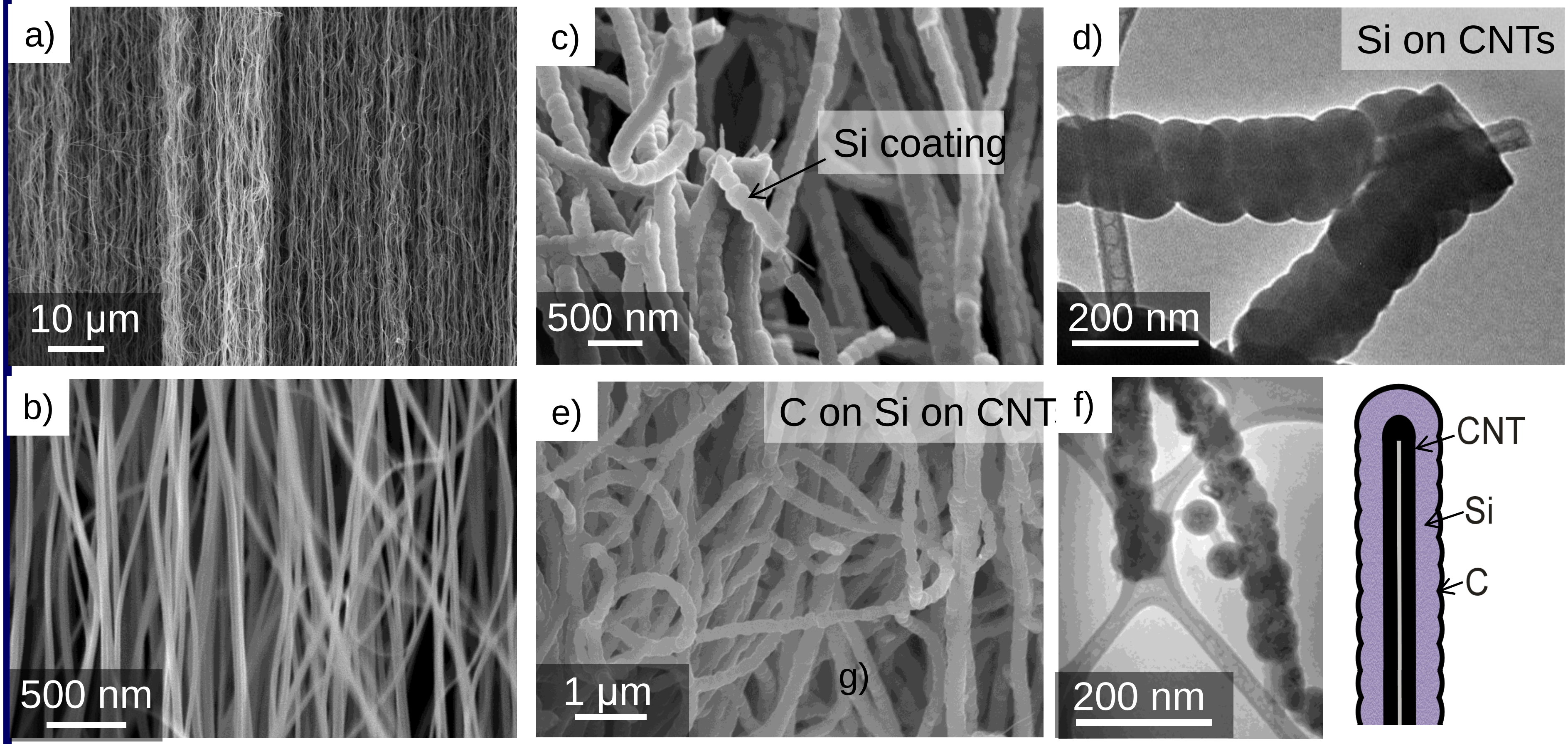
- Tube diameter: 30 nm
- Growth on wafers of up to 4 " possible
- Tube length synthesized: 0.2-2 mm
- Growth time: **2-10 min** for tubes up to 2 mm long
- Can be transferred to Cu foil (or any other) current collectors



Patent pending

Evanoff, K. et. al, ***Advanced Materials***, 24(4), p. 533, 2011

Si- coated Vertically Aligned CNT Anodes

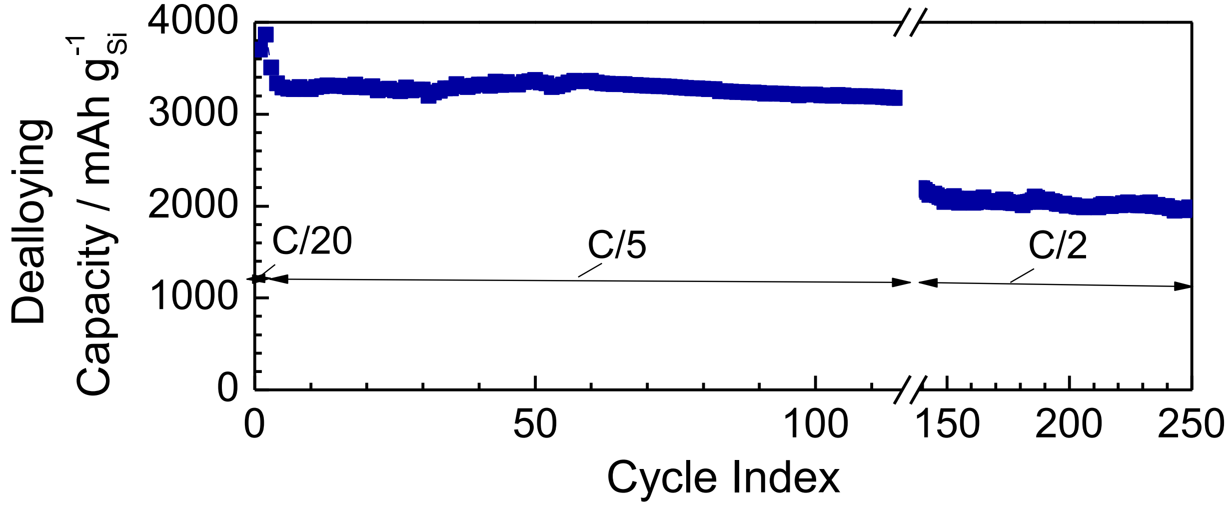


Si coating deposition via CVD (SiH_4 decomposition)

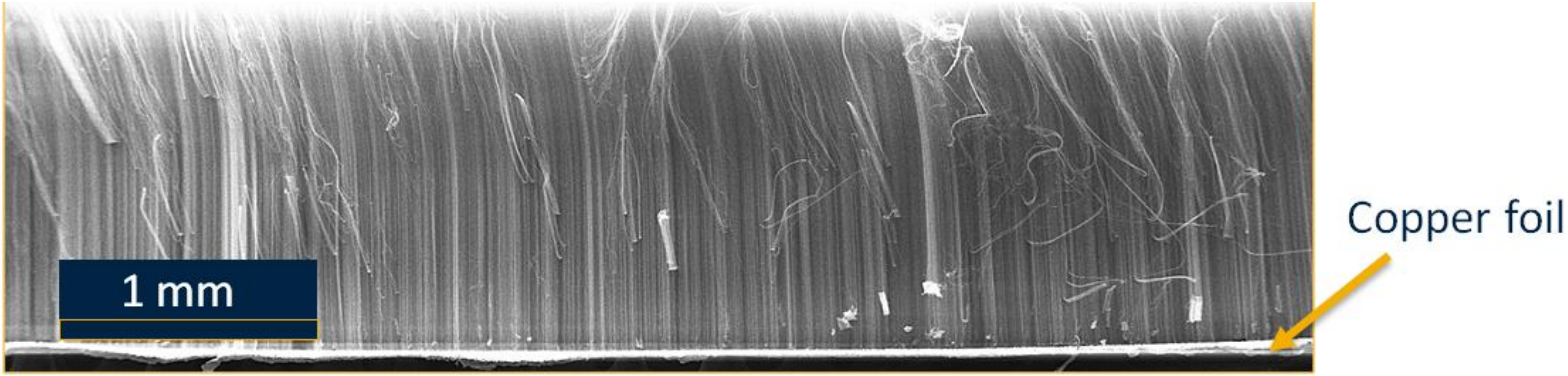
Patent pending

Evanoff, K. et. al, ***Advanced Materials***, 24(4), p. 533, 2011

Si- coated Vertically Aligned CNT Anodes



- ✓ Excellent stability of C-Si-CNT anode
- ✓ Ultra-high anode capacity



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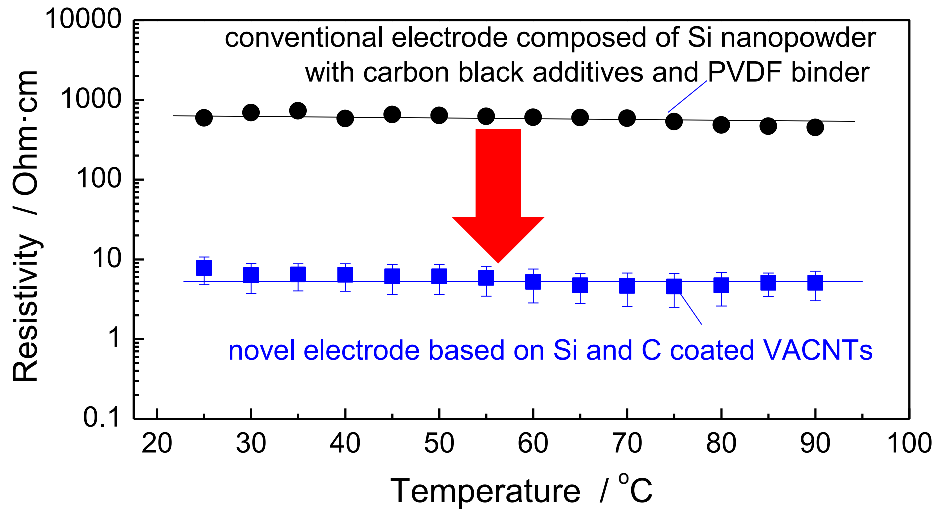
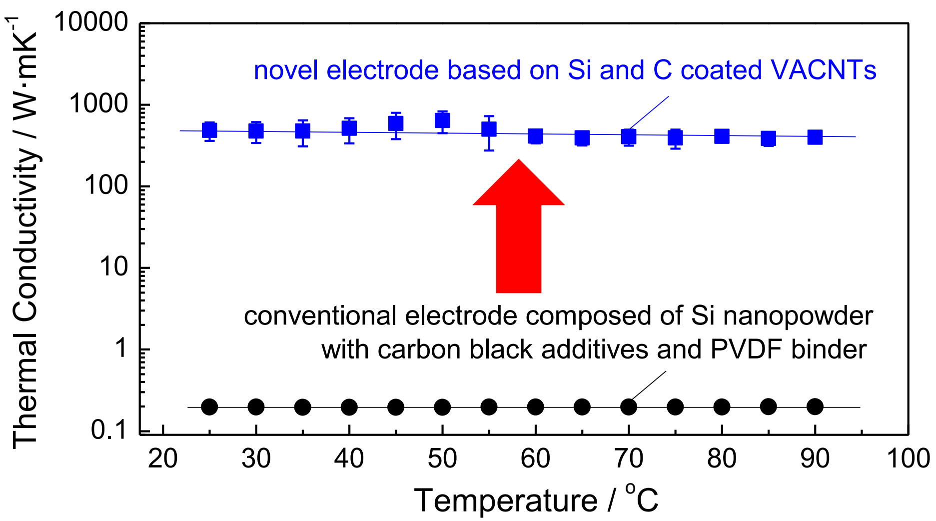
Si-coated Vertically Aligned CNT Anodes



✓ <u>> 100 times lower electrical resistance</u> than that of nanopowder electrode with much higher density but comparable thickness

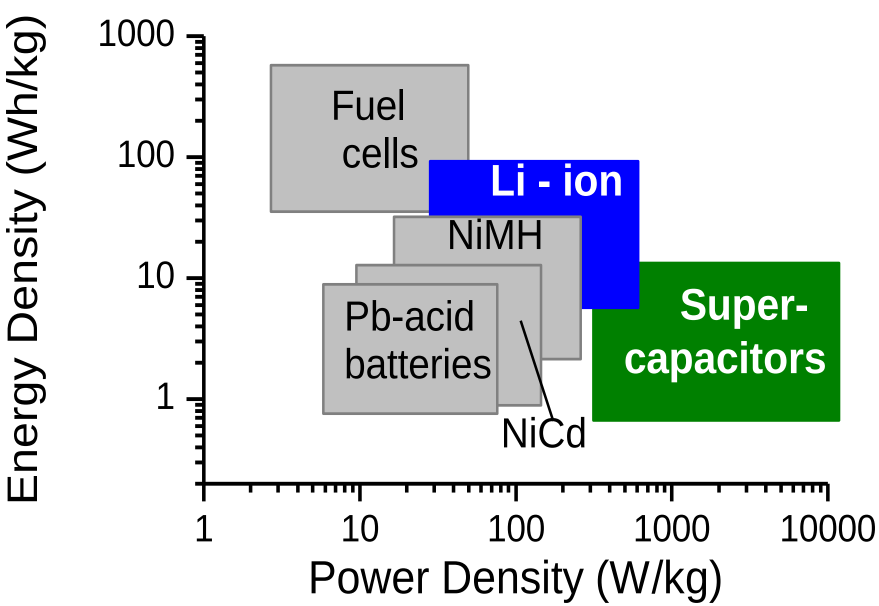


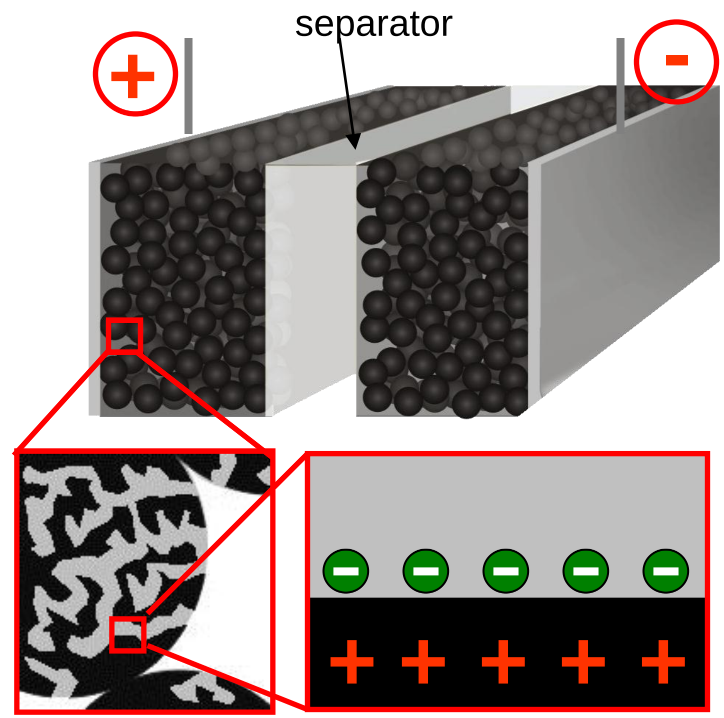
✓ <u>> 1000 times higher thermal conductivity</u> as compared to nanopowder electrode with much higher density but comparable thickness

✓ Excellent thermal properties of the CNT-Cu interface

Evanoff, K. et. al, ***Advanced Materials***, 24(4), p. 533, 2011

Supercapacitors





- **Charge storage:**
  - electrical double-layer (EDLC)
  - fast and reversible faradaic redox reaction (pseudocapacitance)
- **Energy storage depends on the ability of electrode to adsorb electrolyte ions under the applied potential**

Supercapacitors

Routes for Higher Energy Density:

due to packaging, two C in a series etc.

Energy in supercapacitor device $E \approx \frac{CV^2}{2} \cdot \frac{1}{8}$

Capacitance (C) :

(a) 6-30 uF/cm^2 in carbon

(b) up to 200 uF/cm^2 in functionalized carbon

(c) up to 200 uF/cm^2 in transition metal oxides

(semi-bulk / surface layer storage possible)

(d) up to 200 uF/cm^2 in conductive polymers

(semi-bulk / surface layer storage possible)

Limitations of Transitional Metal Oxides and Conductive Polymers:

(a) low electrical conductivity

(b) low surface area

(c) (for conductive polymers): low stability

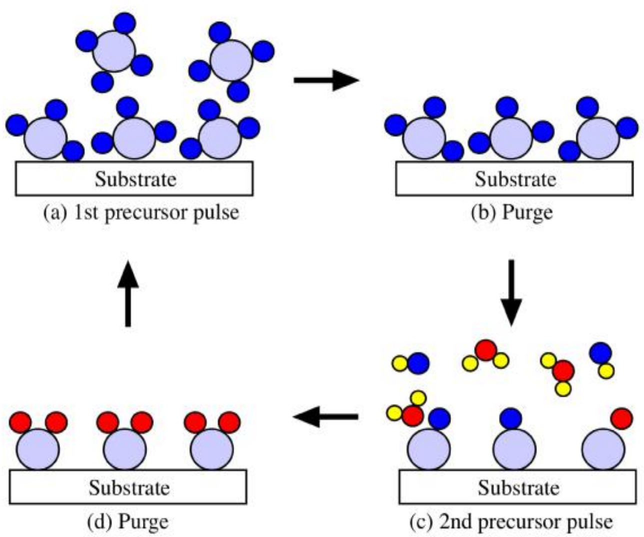
Metal Oxide / CNT Fabric for Supercapacitors

Advantages and Limitations of Transition Metal Oxide-based Supercapacitors

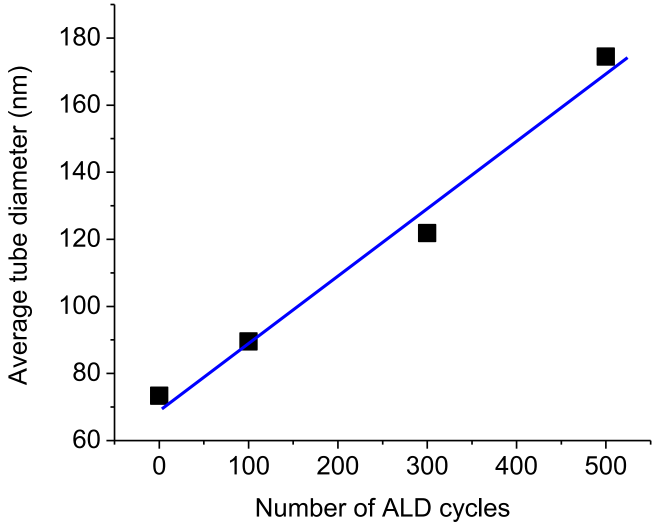
- Low cost transition metal oxides, which offer high specific capacitance (pseudocapacitance), are bad electrical conductors

Project Idea: Utilize Atomic Layer Deposition (ALD) to deposit thin layers of Metal oxide on CNT and other porous carbons

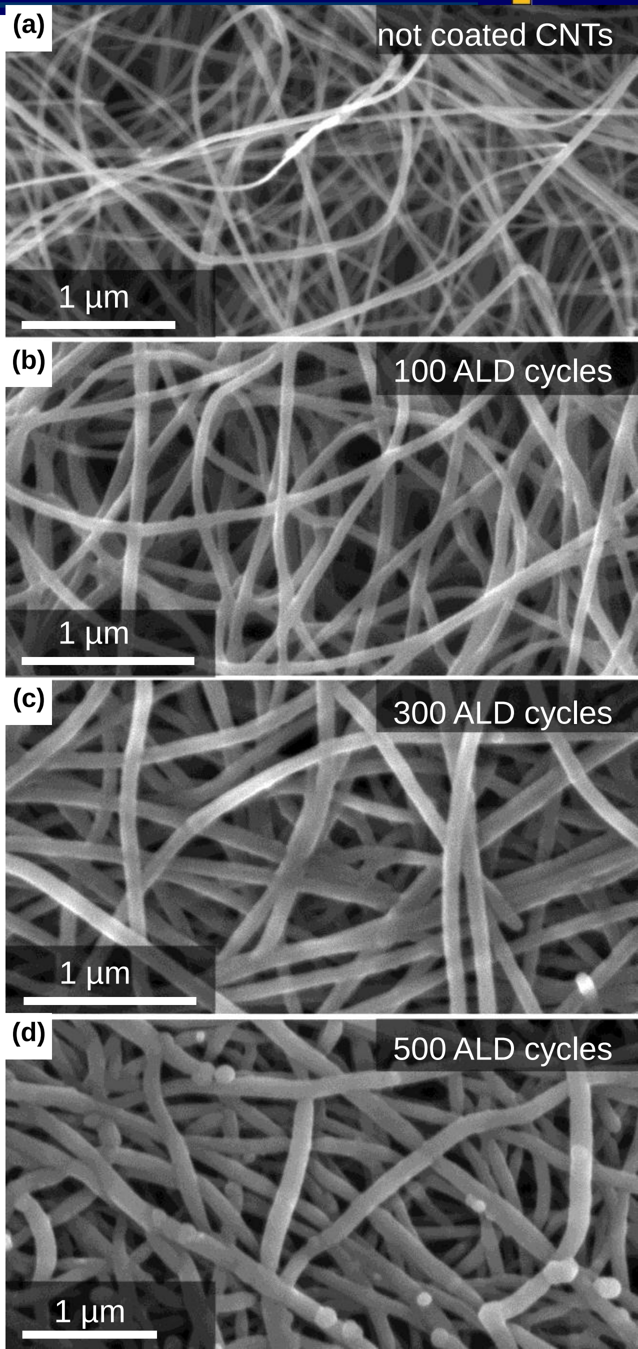
- Precursor and other sources vapors are pulsed into the chamber one at a time, separated by purging or evacuation periods
- Pulse step deposits a sub-monomolecular layer of the precursor onto the substrate
- Purge or evacuation step limits the reaction to the surface by removing the excess reaction gases



Metal Oxide / CNT Fabric for Supercapacitors



Coating thickness increases at **0.1nm/cycle**



- In an ideal case ALD is a surface-limited process, the average coating thickness or the average tube diameter should increase proportionally to the number of the ALD cycles

- An ImageJ software analysis of multiple SEM micrographs reveals linear increase in the average tube diameter with the number of ALD cycles, suggesting that the time allocated for the diffusion of the precursor gases into the porous structure in each cycle was sufficient for the reaction to be surface kinetics-controlled

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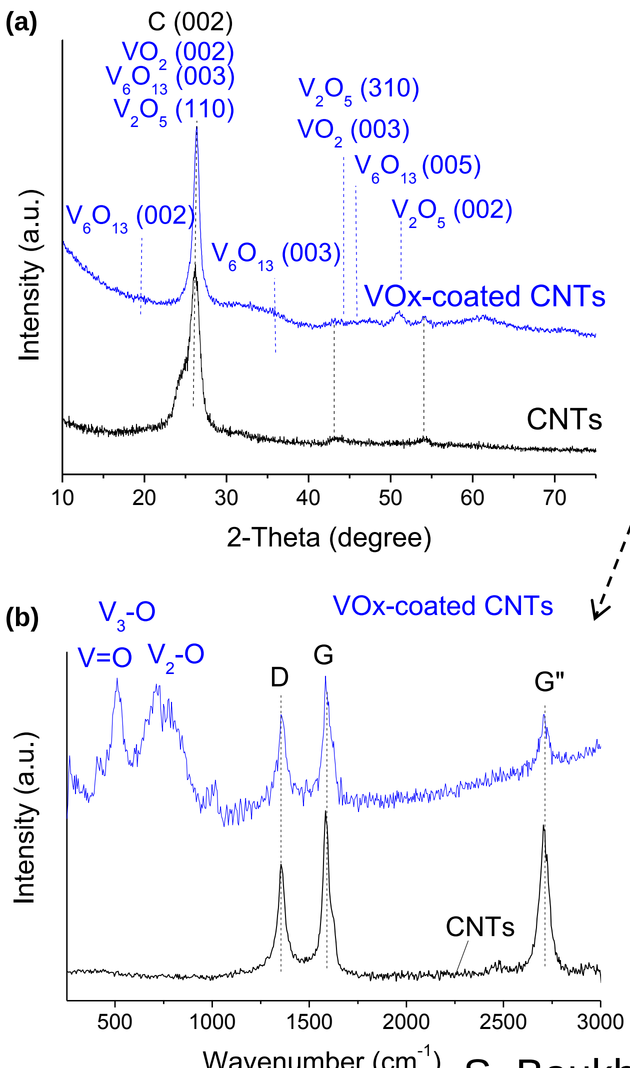

- Produced electrodes are dried at 170 C
- ALD coatings exhibit highly disordered microstructure and contain a range of stoicheometries (particularly evident from Raman spectroscopy measurements)
- V=O bonds are present in **VO_2, V_2O_5**, and **V_2O_3**. Triply coordinated V_3-O bonds only appear in the chemical structure of V_2O_5, while doubly coordinated V_2-O bonds are present in the chemical structure of VO_2 and V_2O_3.

S. Baukhalfa, K. Evanoff and G. Yushin, ***Energy & Env. Science,*** 2012

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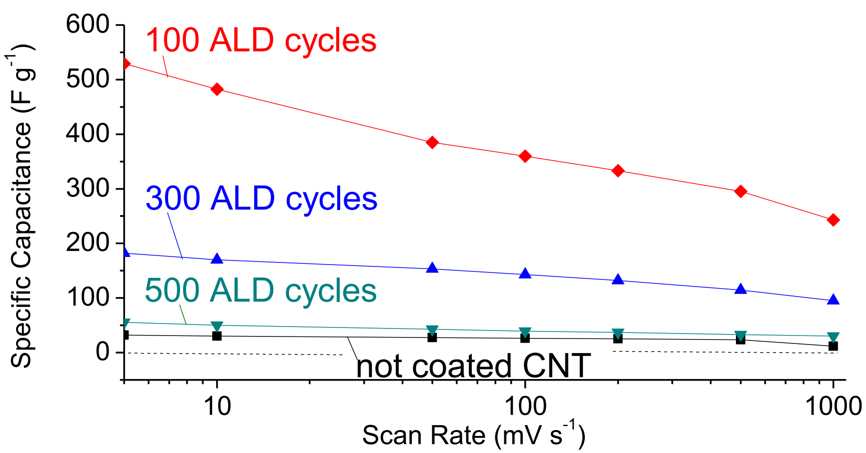
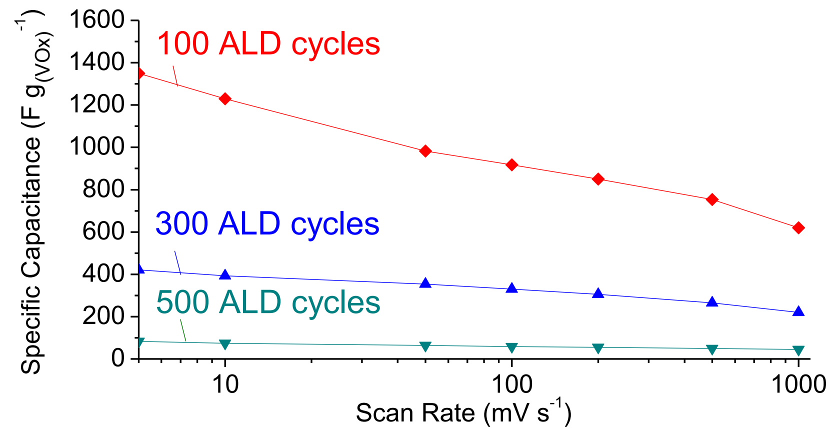
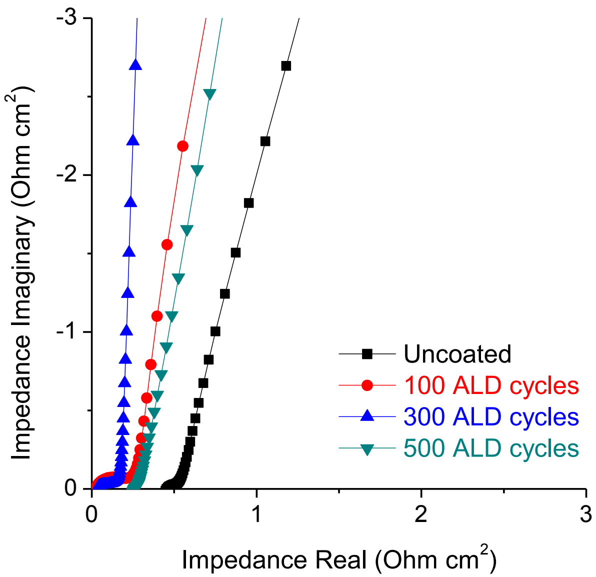




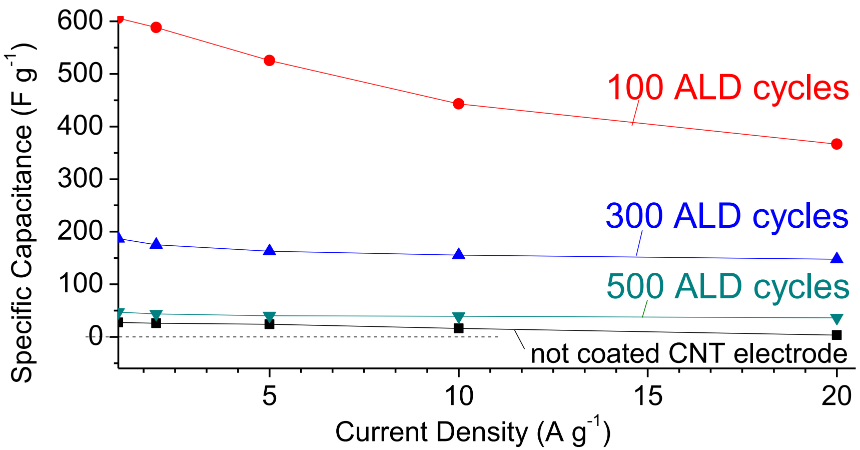


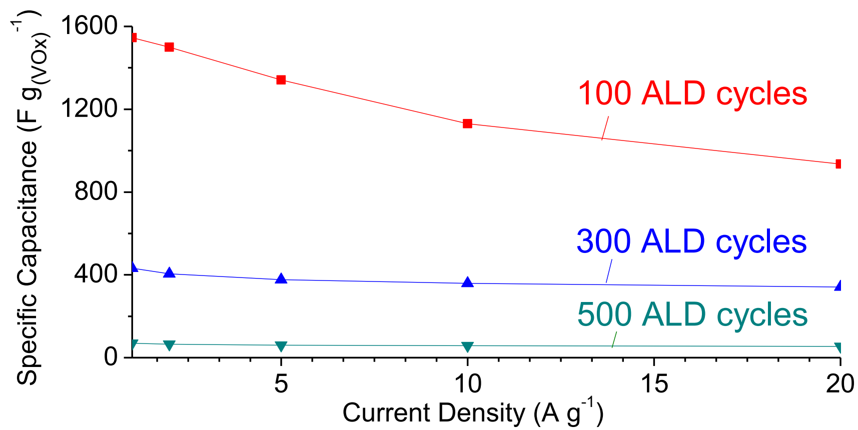
- Symmetric cell (coin cell); Electrode thickness: 100 µm
- Electrolyte: 6M LiCl (aqueous electrolyte)
- Capacitance normalized by the total mass of the composite

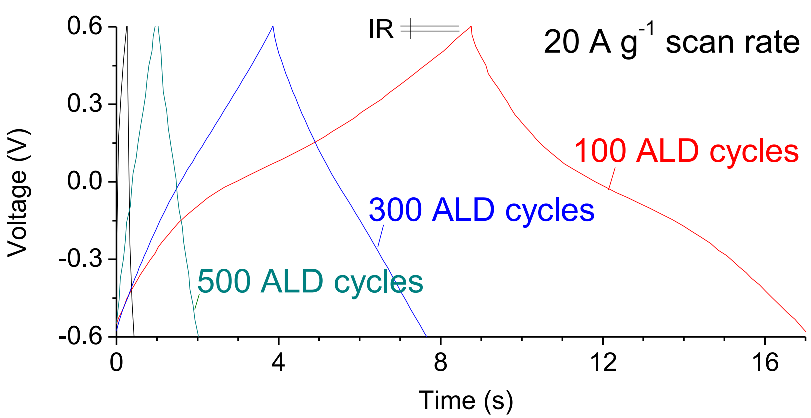
- Vanadium oxide capacitance > 1300 F/g
- ESR of the VOx-coated CNTs is very low (0.02 Ohm cm^2)

S. Baukhalfa, K. Evanoff and G. Yushin, ***Energy & Env. Science,*** 2012

Metal Oxide / CNT Fabric for Supercapacitors



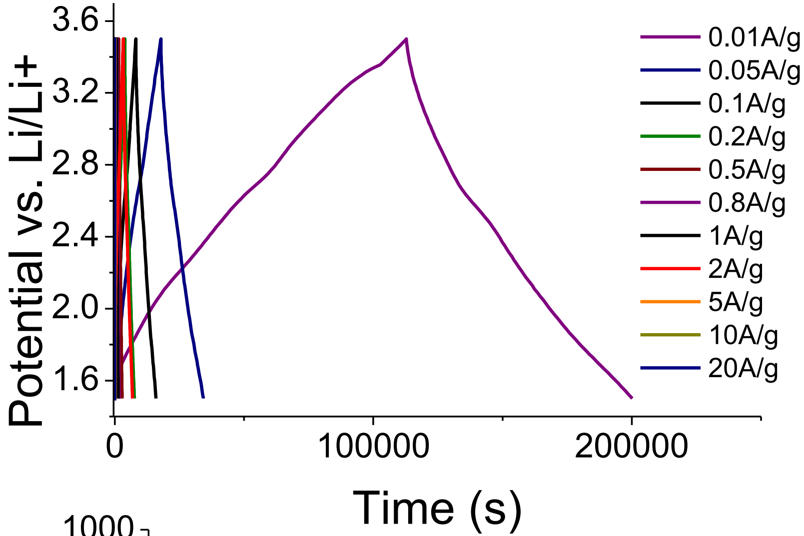


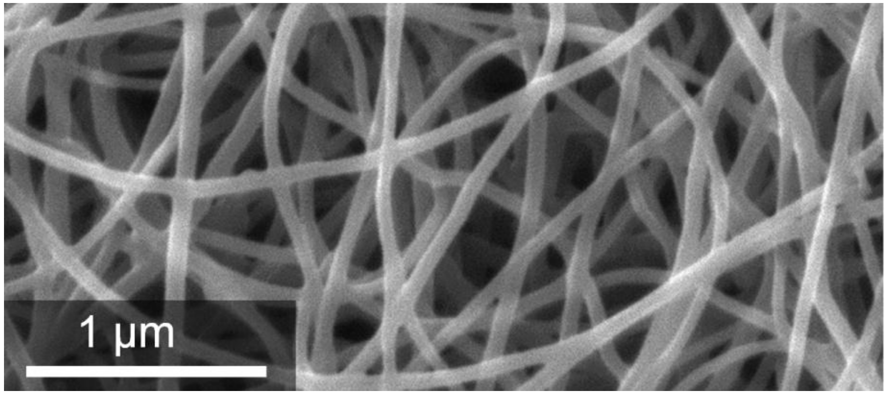


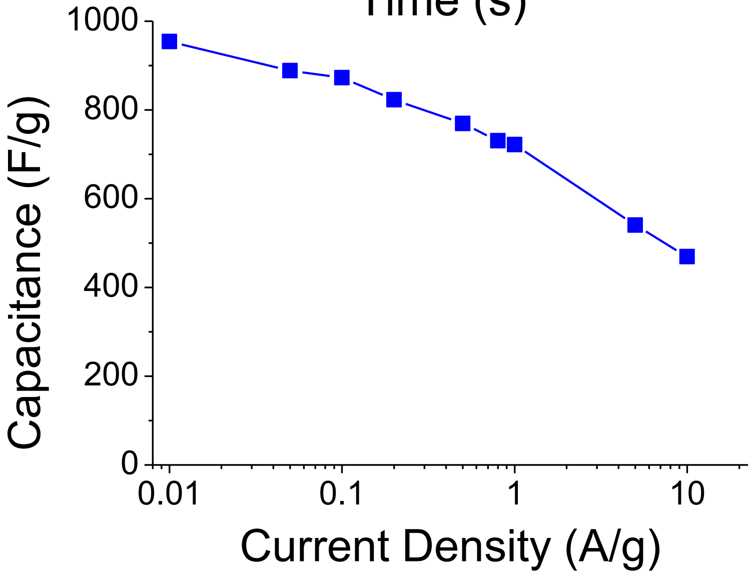
- Vanadium oxide capacitance > 1000 F/g at very high current density of 20 A/g
- Very small IR drop at 20 A/g

S. Baukhalfa, K. Evanoff and G. Yushin, ***Energy & Env. Science,*** 2012

Metal Oxide / CNT Fabric for Supercapacitors (organic electrolytes)







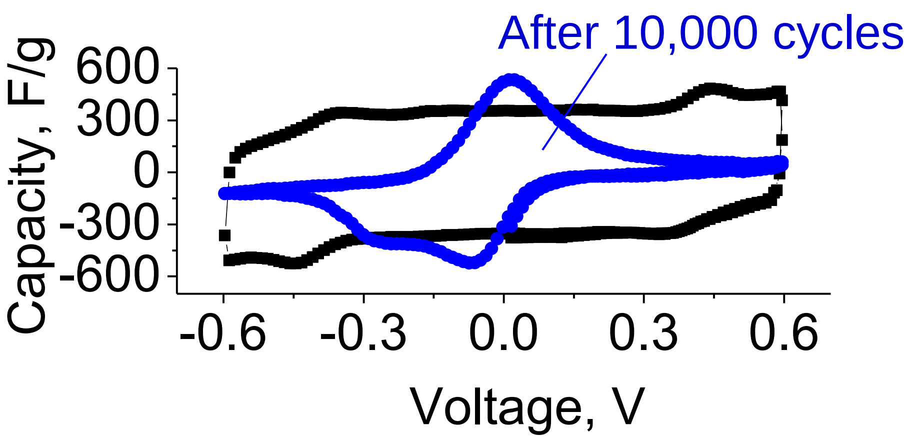
Organic Electrolyte: 1M $LiPF_6$ in the mixture of carbonates (EC:DEC:DMC=1:1:1)

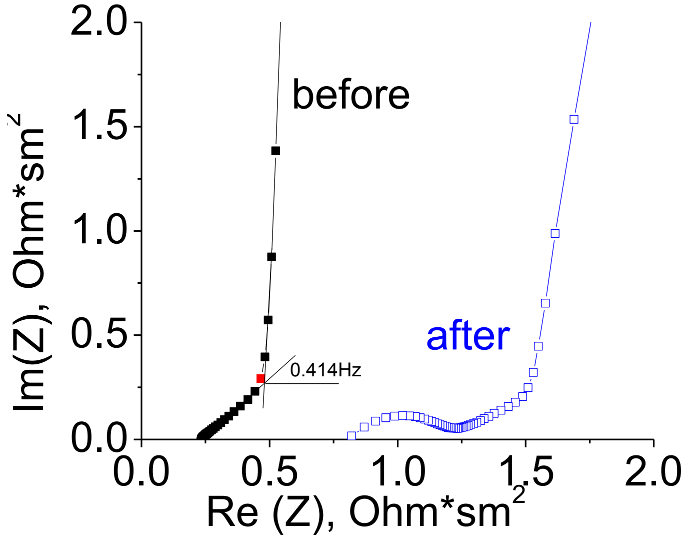
Test configuration: two-electrode cell vs. Li foil counter electrode

- Extremely promising performance (outstandingly high capacitance values)!!!
- Good rate capability
- In the future studies will attempt to use PC as a solvent to further improve the cell rate capability

Polyaniline (PANI) for Supercapacitors

Regular PANI



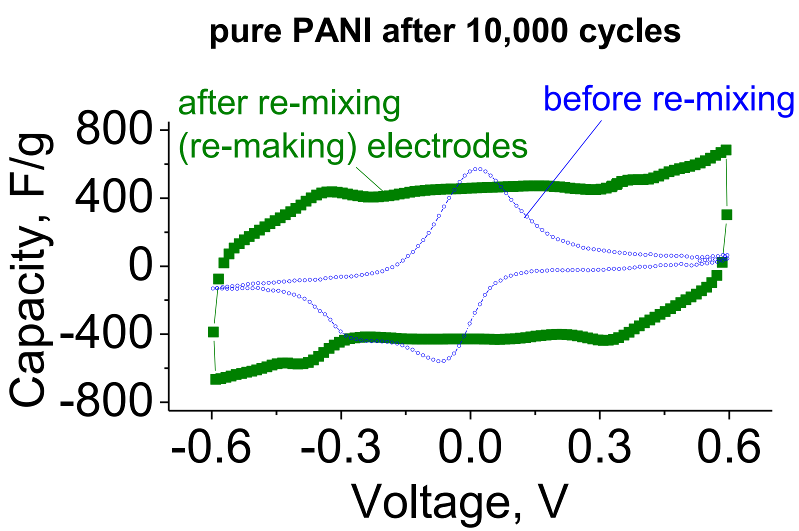


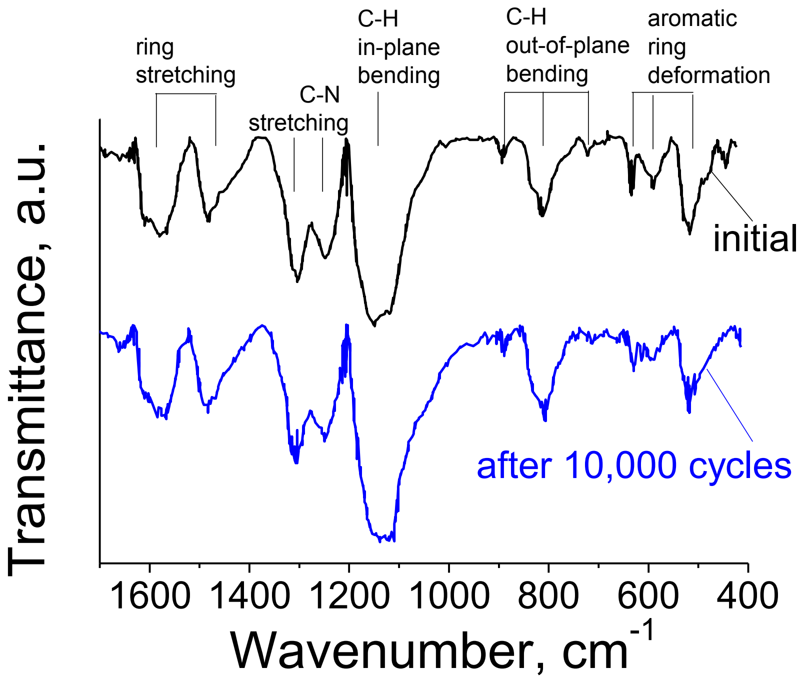
- PANI is inexpensive, conductive polymer with high specific capacitance
- Regular PANI electrodes show rapid performance degradation
- After 10,000 cycles dramatic decrease in capacitance and increase in resistance is observed (particularly at high potentials)

I. Kovalenko, et. al, ***Advanced Func. Materials***, 2010

Polyaniline (PANI) for Supercapacitors

Regular PANI



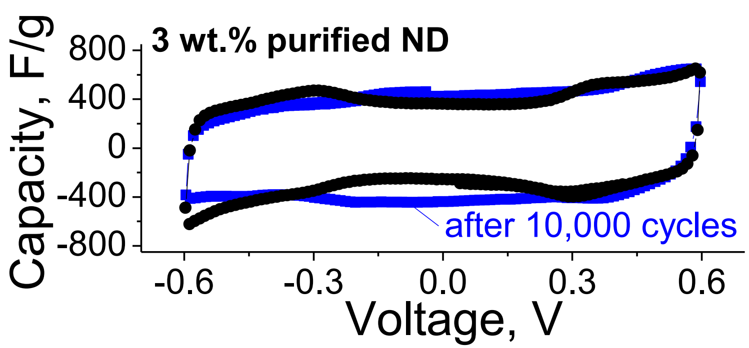


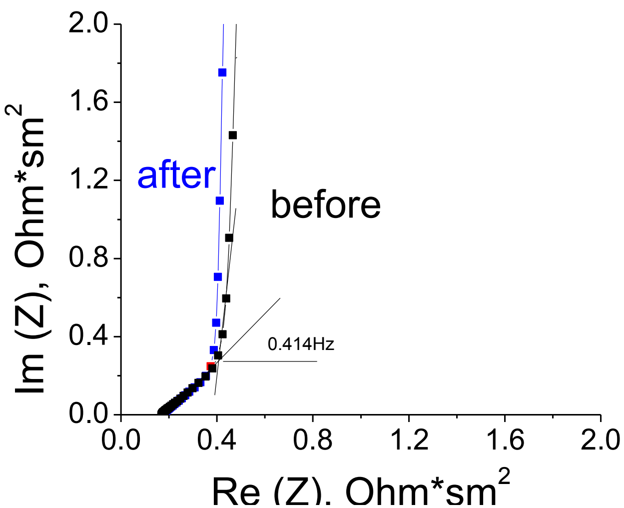
- Performance can be restored after re-mixing the electrodes with a binder
- No chemical modification detected after 10,000 cycles

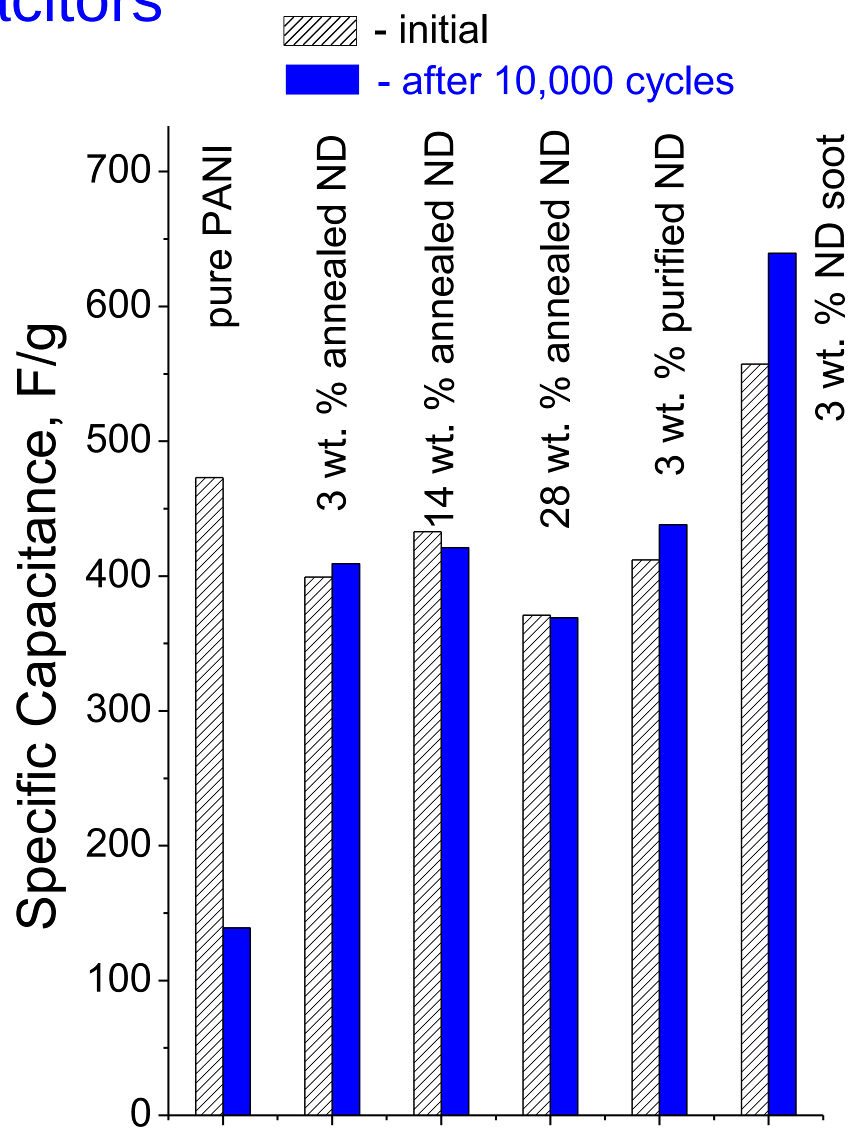
I. Kovalenko, et. al, ***Advanced Func. Materials***, 2010

Nanodiamond (ND)-Embedded Polyaniline (PANI) for Supercapacitors

Aqueous electrolyte



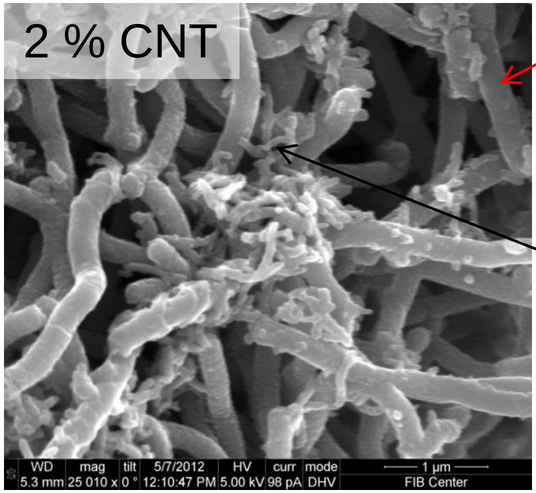




I. Kovalenko, et. al, ***Advanced Func. Materials***, 2010

PANI / CNT Fabric for Supercapacitors

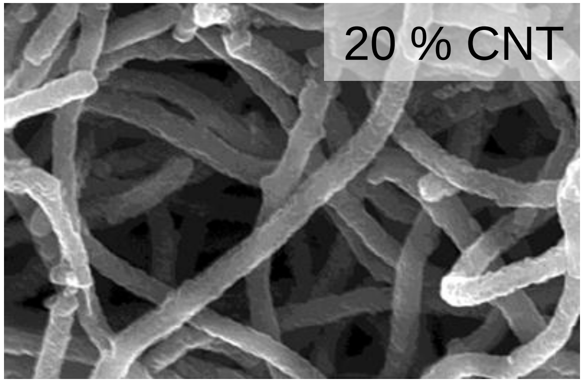
(work in progress)

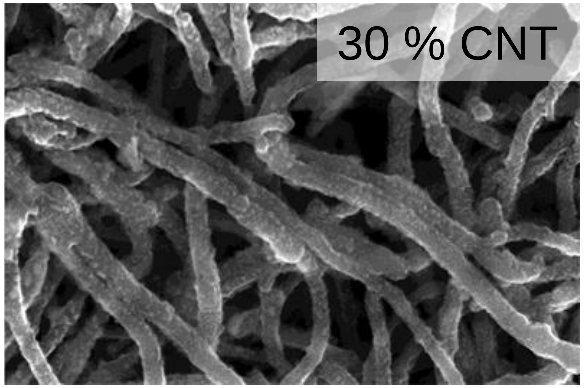


PANI nucleated on the CNT surface

PANI nanoparticles

- low wt. % CNT: individual PANI nanoparticles remaining

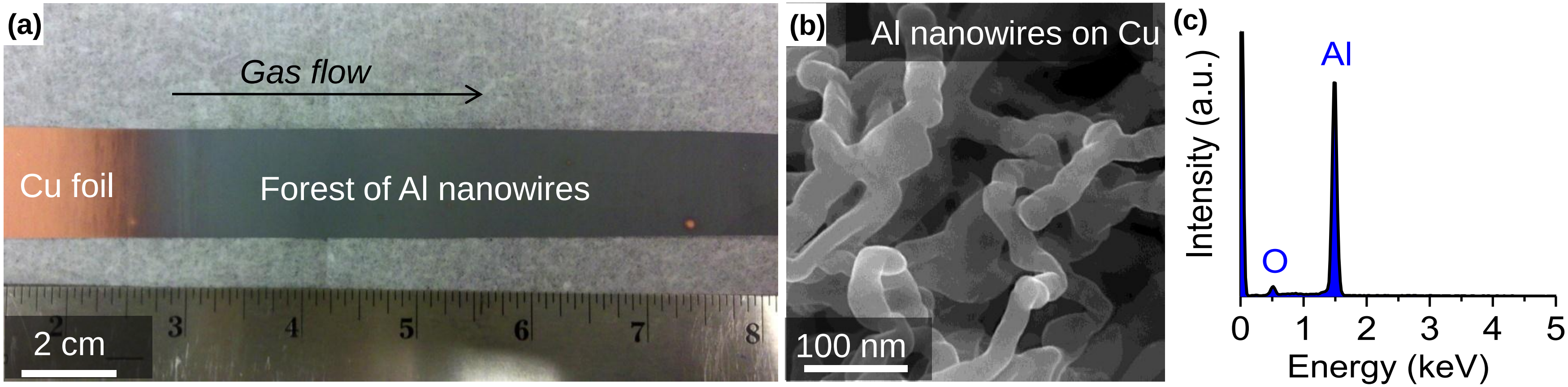




- high wt. % CNT: uniform PANI coating on CNTs

Catalyst-Free Al Nanowire Growth by CVD

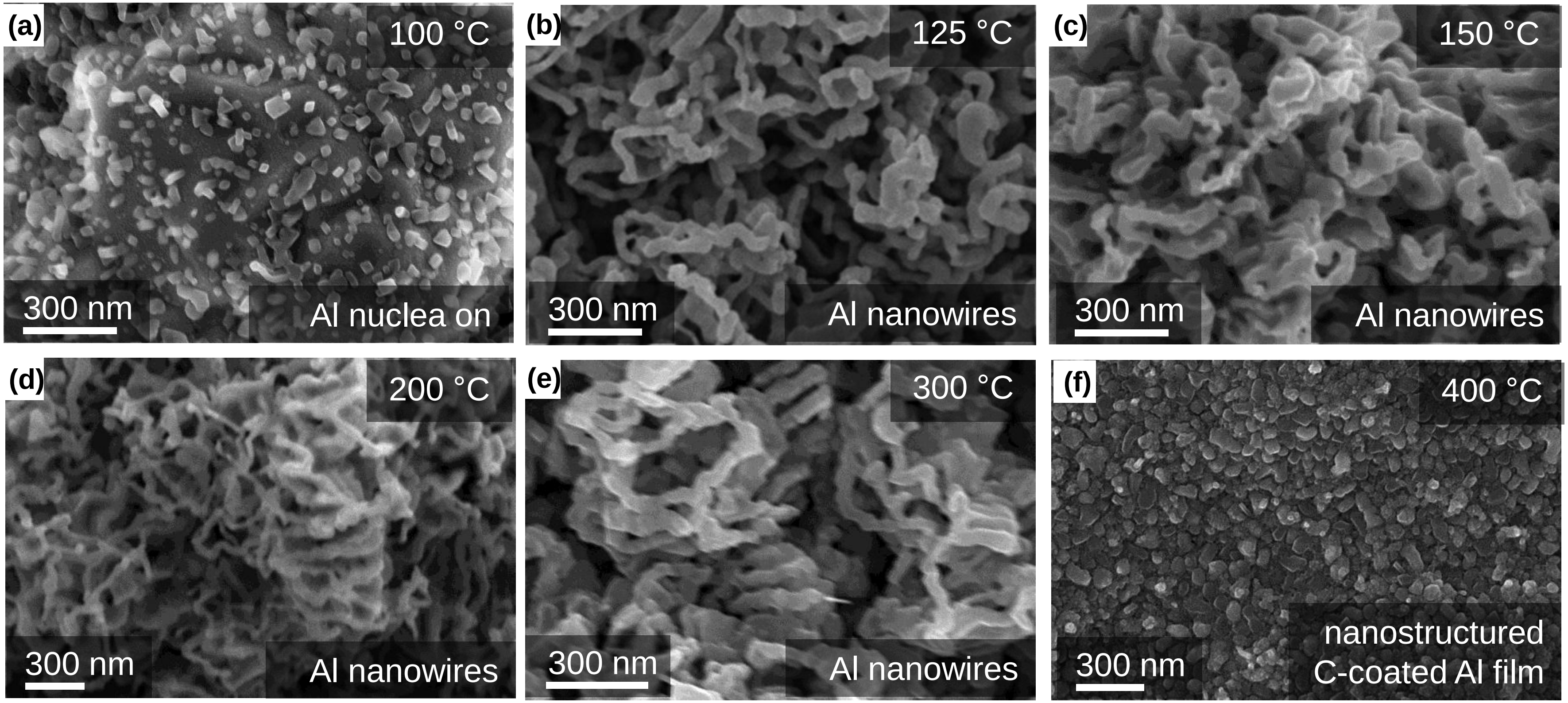
- Limitation of the CNT:
  - low DC conductivity (compared to Al and Cu)
  - low concentration of dangling bonds
- Metal nanowires:
  - typically grown electrochemically using AAO template
  - CVD growth (as CNTs) might offer more scalable process



- Trimethylamine alane (TMAA) as an organometallic CVD precursor
- Catalyst-free

J. Benson et al., ***ACS Nano,*** *6* (1), p 118, 2011

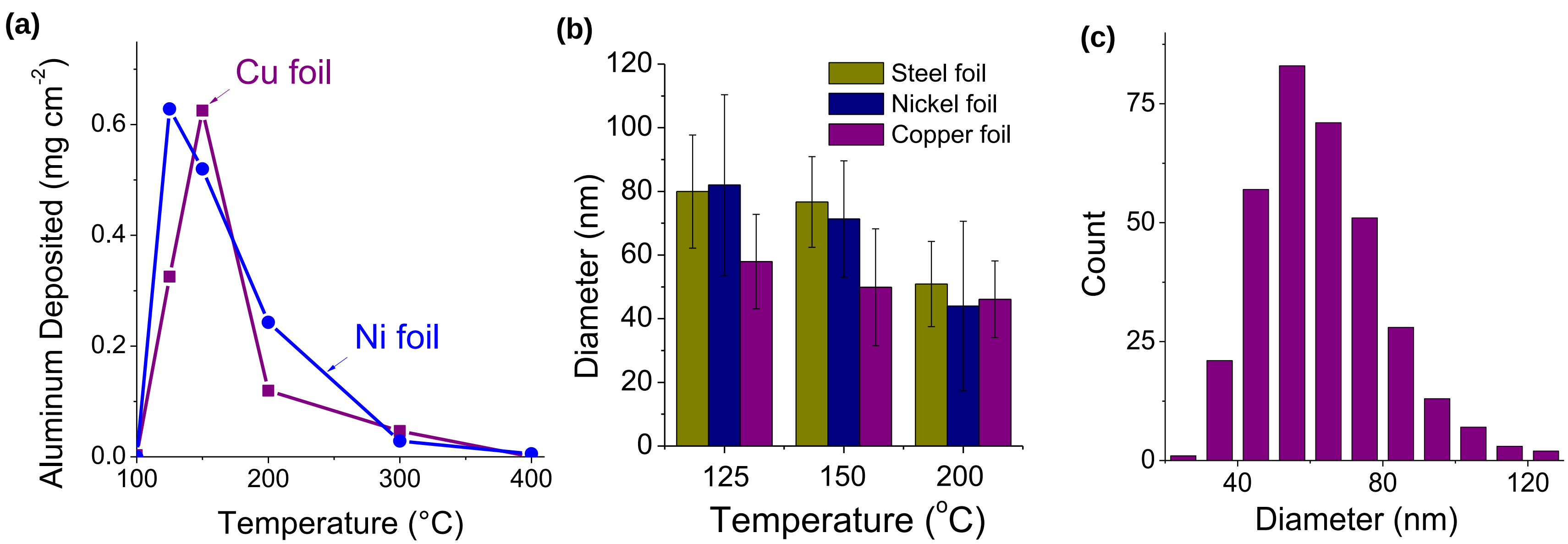
Catalyst-Free Al Nanowire Growth by CVD



- Trimethylamine alane (TMAA) as an organometallic CVD precursor
- Catalyst-free
- Low synthesis temperature: 100-300 °C

J. Benson et al., ***ACS Nano,*** *6* (1), p 118, 2011

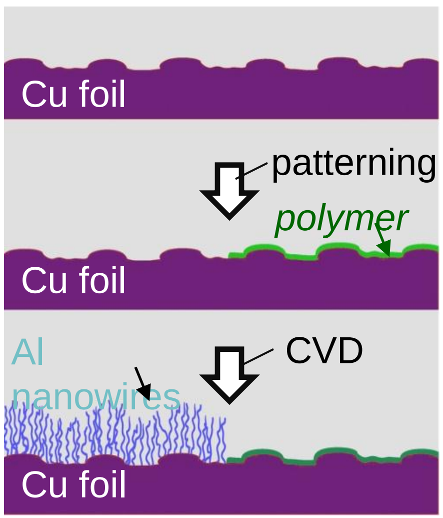
Catalyst-Free Al Nanowire Growth by CVD

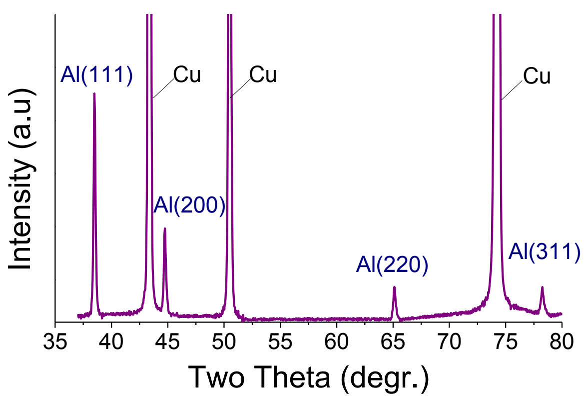


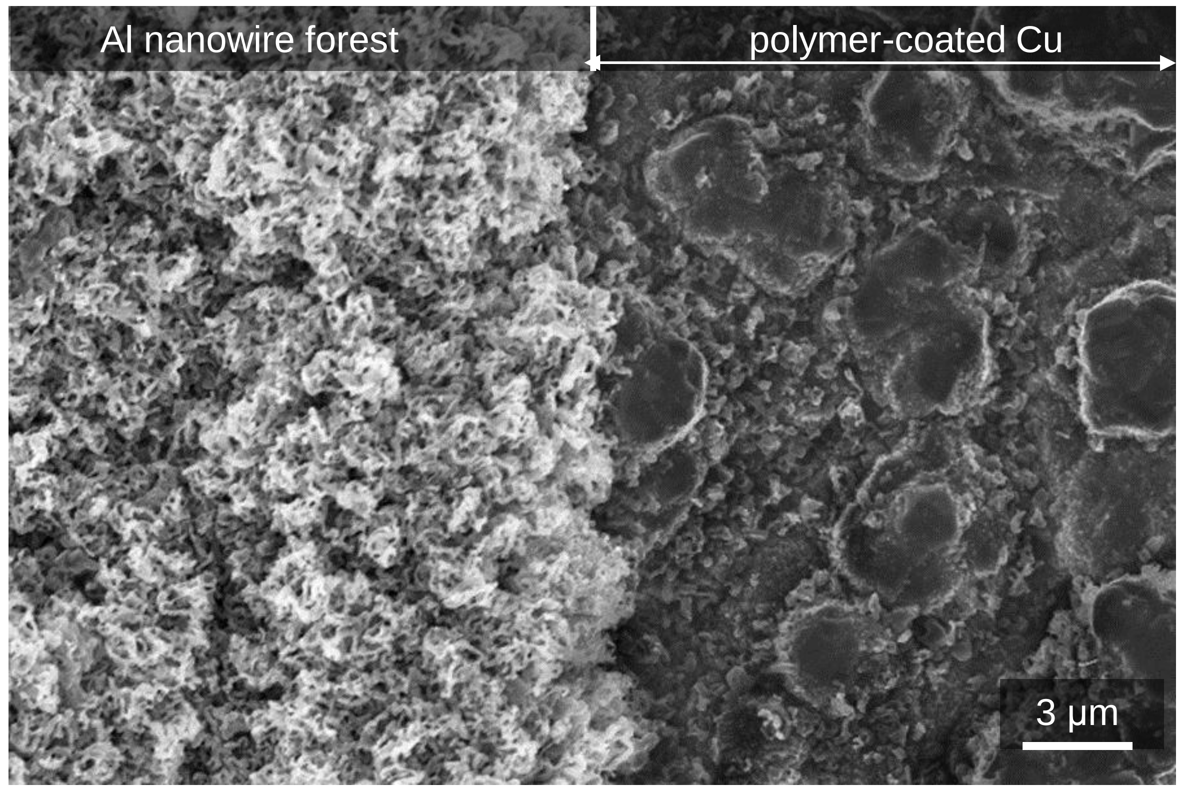
- ➢ Narrow diameter distribution
- ➢ Low temperature (100-200 °C)
- ➢ Uniform diameter along the length of the nanowires; no increase in the nanowire diameter with time, suggesting tip-based growth (likely due to the self-catalytic type of reaction involved)

J. Benson et al., ***ACS Nano,*** *6* (1), p 118, 2011

Catalyst-Free Al Nanowire Growth by CVD



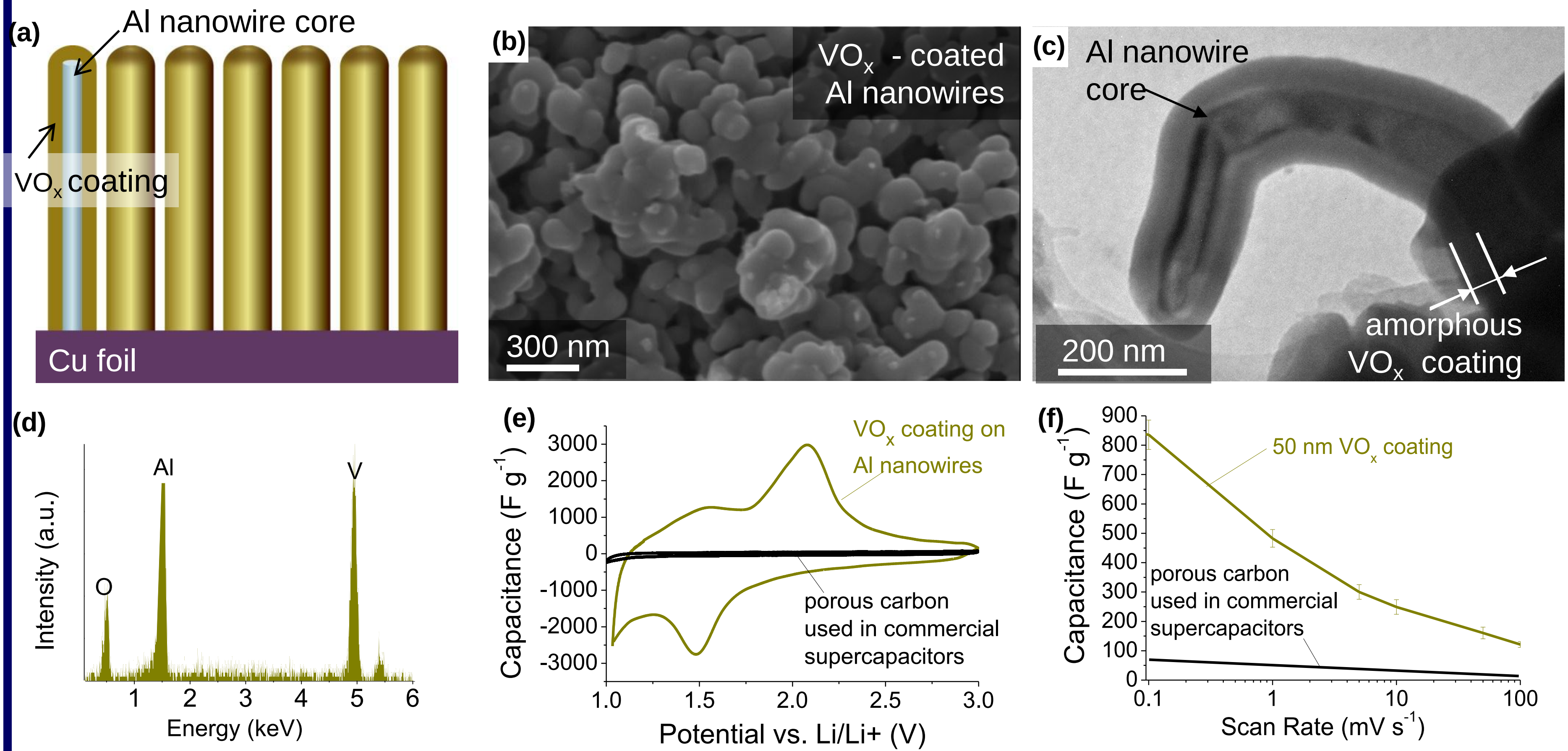




- Polymer layer on the foil surface prevents Al nanowire growth. Therefore, patterned growth becomes feasible

J. Benson et al., ***ACS Nano,*** *6* (1), p 118, 2011

ALD-coated Al Nanowires



- Battery-like AND pseudocapacitor-like behavior
- Gravimetric capacitance of up to 887 F/g is <u>4-10 time higher</u> than C
- Volumetric capacitance of 1390-1950 F/cc is10-40 times higher than that of C in the same electrolyte

J. Benson et al., ***ACS Nano,*** *6* (1), p 118, 2011

Acknowledgement

- Dr. “Les” Lee
- Collaborators (Prof. Igor Luzinov, Dr. Jud Ready, Dr. Zdyrko, NanoComp, *others*)

Support

Disclosure

➢ Mentioned Georgia Tech patents have been licensed to Sila Nanotechnologies, Inc.; Dr. Yushin & GT is a stock holder in Sila